



This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

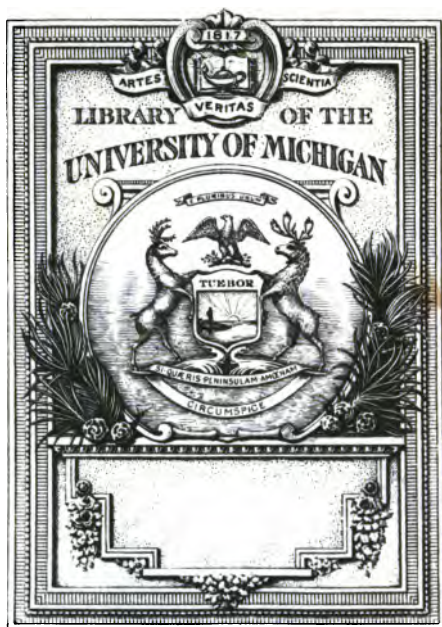
Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

- + *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.
- + *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.
- + *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.
- + *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at <http://books.google.com/>

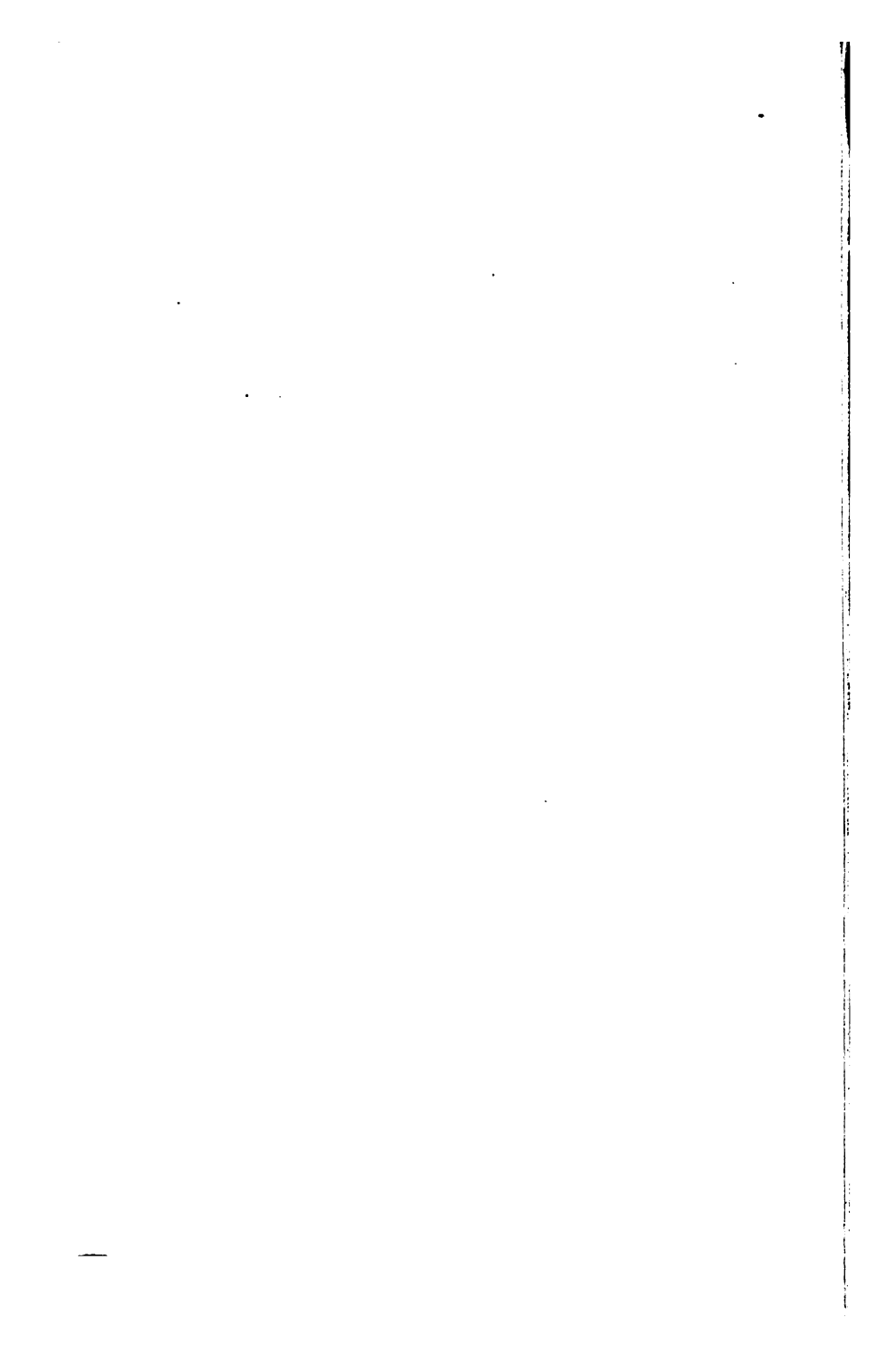


1000000

GD

537

11 26



LABORATORY COURSE
IN
ELECTROCHEMISTRY

McGraw-Hill Book Company

Publishers of Books for

Electrical World	The Engineering and Mining Journal
Engineering Record	Engineering News
Railway Age Gazette	American Machinist
Signal Engineer	American Engineer
Electric Railway Journal	Coal Age
Metallurgical and Chemical Engineering	Power

LABORATORY COURSE IN ELECTROCHEMISTRY

BY
OLIVER P. WATTS, PH. D.
ASSISTANT PROFESSOR OF APPLIED ELECTROCHEMISTRY
THE UNIVERSITY OF WISCONSIN

FIRST EDITION

McGRAW-HILL BOOK COMPANY, INC.
239 WEST 39TH STREET, NEW YORK
6 BOUVERIE STREET, LONDON, E. C.
1914

COPYRIGHT, 1914, BY THE
MCGRAW-HILL BOOK COMPANY, INC.

THE MAPLE PRESS YORK PA

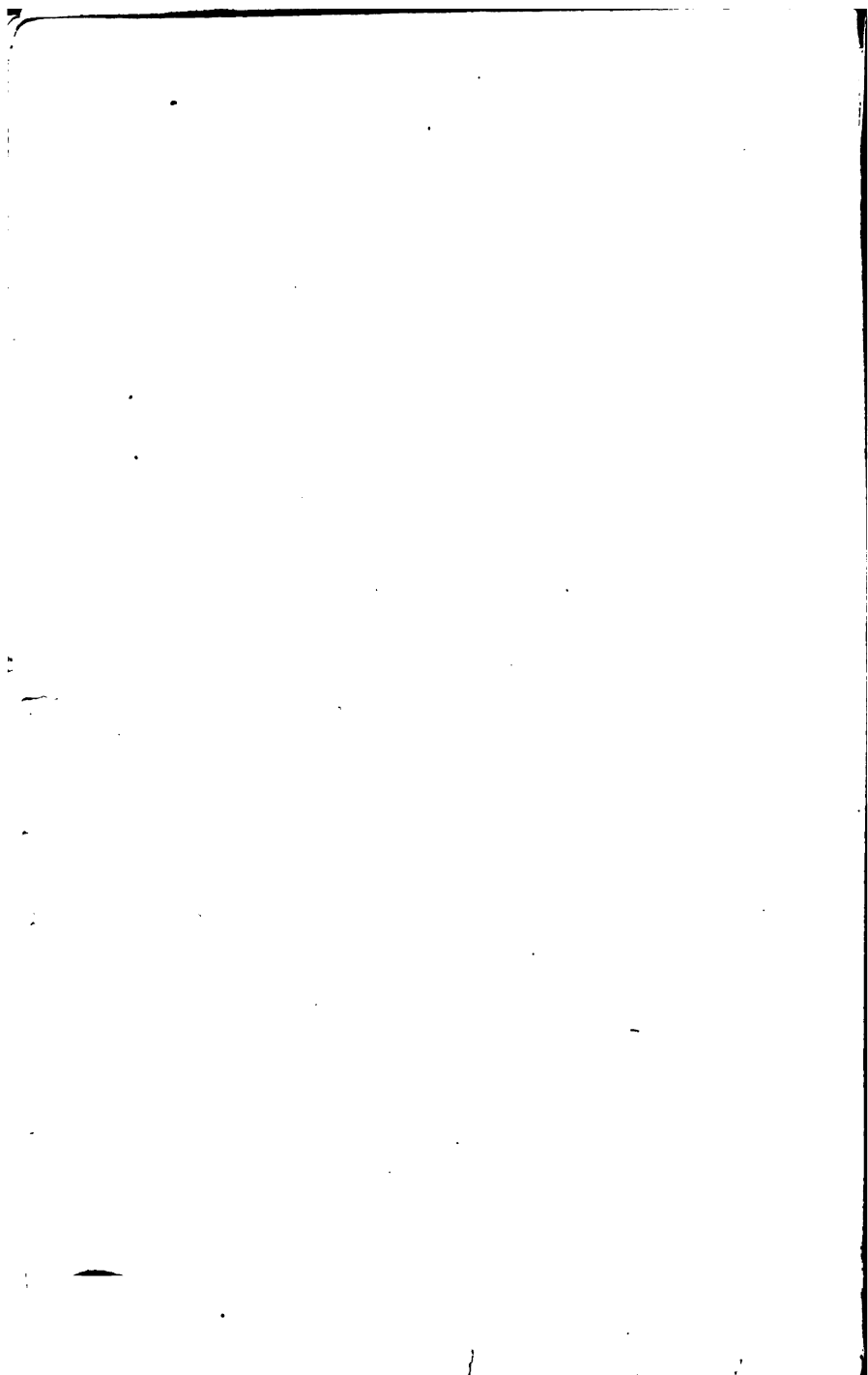
PREFACE

This laboratory manual has been designed primarily for use in the author's classes in the University of Wisconsin, and embodies the notes originally prepared by C. F. Burgess, former head of the Chemical Engineering department of the University, together with many new experiments and much additional material. It is hoped that it may prove a useful handbook in applied electrochemical courses elsewhere than at Wisconsin.

Thanks are due to Mr. C. F. Burgess for the use of his notes, and to Mr. Claude N. Hitchcock for the drawings which illustrate the text, and for the use of figures 13, 14 and 15, which were originally published in his paper upon Polarization Single Potentials (vol. 25, Transactions of Americal Electrochemical Society).

O. P. W.

Sept., 1914.



CONTENTS

	PAGE
INTRODUCTION.	1
LABORATORY EQUIPMENT.	2
INSTRUCTIONS FOR STUDENTS	5
QUALITATIVE EXPERIMENTS ON ELECTROLYSIS	10
SPECIFIC RESISTANCE.	13
POLARIZATION	15
FARADAY'S LAW	29
POTENTIAL AND ELECTROMOTIVE FORCE	33
DISCHARGE POTENTIALS	56
OVERVOLTAGE	58
PASSIVE STATE	58
CORROSION OF METALS	60
ELECTROLYTIC SEPARATION OF METALS	63
ELECTROLYTIC ANALYSIS.	66
INTERMEDIATE ELECTRODES.	69
ELECTROPLATING BATHS.	72
SOLUTIONS FOR COLORING AND OXIDIZING METALS.	79
PRINCIPLES OF ELECTRODEPOSITION	84
CLEANING AND POLISHING	89
NICKEL PLATING	93
COPPER PLATING	95
THE DEPOSITION OF ALLOYS	97
BRASS PLATING	100
SILVER PLATING	101
EXPERIMENTS IN PLATING	103
OXIDATION AND REDUCTION.	121
OTHER ELECTROLYTIC PREPARATIONS	132
APPENDIX	138
INDEX	147

A LABORATORY COURSE IN ELECTROCHEMISTRY

INTRODUCTION

The experiments in this manual have been chosen to illustrate the general principles which underlie the more important applications of electrochemistry. No attempt has been made to adapt commercial processes to the laboratory, although a few experiments of this character, in which the apparatus lends itself readily to laboratory use, have been included. The electric furnace and batteries have been omitted, since they are studied as separate courses by the author's classes. Electrolytic analysis has been developed to such an extent that it now constitutes a study by itself, and cannot be adequately treated in a book on electrochemistry in general. Although a few simple experiments are given, the student who wishes to study this branch of electrochemistry is referred to the well-known texts by Smith and Classen.

Even with the above limitations in scope, it will probably be impossible for the student to perform all of the experiments in the time available. It will be found, however, that under many topics the experiments are so similar in nature that the method of operation and the use of the apparatus may be learned from any one of them. It is therefore suggested that in such cases the class or laboratory section work together on the topic, a particular experiment being assigned to one or two students who report their data and conclusions to the class for discussion. All data and results may be recorded in

2 A LABORATORY COURSE IN ELECTROCHEMISTRY

the notebooks, but credited to the observer, so that each student will have a record of the experiments of others as well as of his own.

The laboratory work should be accompanied by lectures, recitations and assigned reading in books and periodicals. The latter is valuable, not only for the information gained, but quite as much for the acquaintance obtained with electrochemical literature and the men who are producing it.

Laboratory Equipment

A brief description of the laboratory equipment which is provided for these experiments may be useful.

The laboratory receives current over three pairs of cables, two from the main switch-board, and one running directly from the storage battery in the basement. The advantage of this direct connection of the battery is that experiments cannot be interrupted by the accidental pulling of the wrong plug from the switch-board. The two pairs of cables from the switch-board are usually connected to 110 volts direct and alternating pressure respectively. From the cables wires are brought down to terminals above and at the back of each student's place at the laboratory desk. The 110-volt direct current can be used only during the day, but the 10-volt battery and alternating pressures are always available. The battery current is used in the majority of experiments, while the alternating current is useful for driving motors and heating electrolytes in experiments that are continued over night.

The storage battery consists of nine sets connected in parallel, each set having five 160 ampere-hour cells in series, making the total capacity 1440 ampere-hours. By means of switches, any number of sets is readily

connected in series for charging. A 6-volt battery of half this capacity would probably prove ample for ordinary demands.

There is available to each student direct current at 10 and 110 volts pressure. Control of either current or E.M.F. as may be required for any particular experiment, is secured by portable rheostats, consisting of small lamp banks, and the ordinary wire-wound rheostats with sliding contacts. About a third of the wire rheostats have resistances high enough to permit their use on the 110-volt circuit.

A second pair of cables from the battery would be an advantage, as one pair could then be reserved for experiments requiring constancy of line voltage, thus avoiding the fluctuations produced by the use of the electric cleaner and similar intermittent high-current work.

Ammeters, voltmeters, rheostats, etc., are kept in cases in the laboratory, from which they are taken by the students at the beginning of the four-hour laboratory period, and returned at its close. Lamp cord, cut to different lengths, with an inch of bare No. 18 copper wire soldered to the ends, is used for electrical connections. This method of distribution and control of current is recommended for its simplicity and economy, and for the practice which it gives the student in setting up electrical circuits and in the control of the electric current. The last feature is especially important.

Ammeters having ranges of 1 and of 10 amperes are most used, although at least one instrument of 50 amperes capacity should be available. Two or three double-scale milliammeters (range 50 and 500) are needed. Although double-scale voltmeters are not so convenient for rapid reading as single-scale instruments, a considerable saving in cost can be effected by their use for a large part of the voltmeter equipment. The two

4 A LABORATORY COURSE IN ELECTROCHEMISTRY

scales should be chosen so that both are capable of direct reading, *i.e.*, the ratio between them should not be 3 to 1 or 30 to 1. Several single-scale instruments with a range of 3 volts are useful for reading low voltages with accuracy. The medium-priced, portable type of instrument is satisfactory for general laboratory use, but several high-grade instruments should be available for research work.

The outfit for measuring potentials consists of a two-dial rheostat¹ of 1000 ohms (American made) with its coils connected for use as a potentiometer. This costs \$42.50. A galvanometer, keyless preferred, costing about \$18, and a strong, well-made, short-circuit key which costs \$6.50, completes the outfit. The cost of this outfit, \$67, is very reasonable when its satisfactory service is compared with that of some cheaper instruments with which the author has had the misfortune to work.

One S.P.S.T., one S.P.D.T., and one D.P.D.T., 15-ampere, porcelain base switch may be fastened permanently to each desk, or they may be mounted together on a single small board, which is put away at the end of each laboratory period, leaving the desks clear.

For small electrolytic cells, plain, heavy, straight tumblers have been found superior to beakers as they are rarely upset or broken. Rectangular glass battery jars of 600 and 1400 c.c. capacity are convenient for electroplating on a small scale. For plating baths of 10 to 100 liters, rectangular acid-proof tanks may be purchased very reasonably directly from the manufacturers of chemical stoneware.

For polishing metals, two or more standard polishing lathes with cloth wheels (bobs) should be provided. The sheet brass or copper used for experiments in electrodeposition must have a smooth surface. To avoid the

¹ Described on page 37.

trouble and expense of cutting down with emery, it is best to buy the sheet metal already polished.

An iron potash tank heated by a steam coil is a necessity for removing grease from large work. If plating is conducted only on a small scale, a thin cast-iron kettle, heated by a laboratory burner, will serve as the potash tank. Either may be used as an "electric cleaner" by connecting the tank directly to the positive battery cable by a *heavy* copper wire, and supporting across the tank, but insulated from it, a 3/8-inch brass rod connected to the negative terminal of the battery. A pole-reversing switch will enable the object to be made cathode or anode at will.

Instructions for Students

"Experience shows that there is a great tendency among those who commence the study of electrochemistry to *slop* through the work. The average student seems to think all that is necessary is to mix his solutions in a more or less accurate manner, and then to switch on the current—the electricity will do the rest. A greater mistake could not be made; unless details of current density, electromotive force, temperature and composition of the electrolyte are carefully attended to, the results will not be such as are expected, or as are set out in the book. Students are very apt to say: 'It is about right,' or 'The results are near enough.' Such workers will never succeed and do not deserve success."—F. M. Perkin in "Practical Methods of Electrochemistry."

A laboratory experiment demands the best efforts of the hand, eye, and brain. It is not sufficient to see that the apparatus is set up exactly as directed, that the electrical instruments are read accurately, that the readings are recorded correctly, and that all questions in the text are answered satisfactorily. Each experiment, in addition to the purpose expressed in its title, should be regarded as an exercise to develop the powers of observa-

6 A LABORATORY COURSE IN ELECTROCHEMISTRY

tion, and as a study of the process of electrolysis; therefore anything new, or of interest to the student should be recorded. To learn how to set up apparatus and to control the electric current for various purposes is also a valuable part of laboratory practice.

Every electric circuit should contain a switch, in order that the circuit may be broken promptly in case of accident, and a rheostat suited to the voltage employed. Knowing the line voltage and the current desired, the resistance required for the rheostat may be calculated from the equation representing Ohm's Law: $R = \frac{E}{I}$, in

which E is the E.M.F. in volts, I is the current in amperes, and R is the resistance in ohms. In connecting a rheostat, great care should be taken to see that at the outset it is adjusted for its *maximum* resistance. Carelessness in this respect may result in the injury, or even in the destruction of the electrical instruments.

Students are expected to report at once any damage to instruments, and are held responsible for repairs.

The polarity of all cable terminals in the laboratory should be plainly marked, and at least one terminal of every ammeter and voltmeter has been marked by the maker. Ammeters should be connected in series, *i.e.*, so that the full current flowing in the circuit must pass through the instrument. Unless otherwise specifically stated, voltmeters should be connected across the two points whose difference of potential it is desired to measure. The positive terminal of the ammeter should be connected to the wire which has come from the positive terminal of the line, and the positive of the voltmeter should go to the anode, *i.e.*, to the side of the electrolytic cell which is connected to the positive of the line.

Before closing the switch, the student should trace out the circuit carefully, to see that the current will go only

A LABORATORY COURSE IN ELECTROCHEMISTRY

where desired, and that the instruments are connected so that the current will enter at their positive terminals. This is best done by starting at the positive terminal of the line and following the circuit by actual physical contact of the hand, through the cell and instruments, around to the negative terminal of the line. For taking down the apparatus there is but one safe rule to follow: after opening the switch, *first disconnect both wires from the line terminals*. This insures that no live wires are on the desk top, and all danger of a short-circuit is avoided.

In order to use electrical instruments intelligently and safely, it is necessary to understand their construction. The principles of operation of the Weston direct-current instruments will be described.

The millivoltmeter is the basis of both the voltmeter and the ammeter. Examination shows that the millivoltmeter consists of a movable coil of very fine wire, to which the needle is attached, carefully pivoted on jewelled bearings between the poles of a permanent magnet. Current enters and leaves the coil through very fine steel springs, one of which is visible at the upper bearing. When current passes through the coil, it sets up a magnetic field, which, reacting with the field of the permanent magnet, turns the coil and moves the needle up the scale. When the current ceases, the springs return the needle to zero. The delicacy of the springs and coil indicate that only extremely small currents can be sent through a millivoltmeter without injuring it.

The voltmeter consists of a millivoltmeter with a resistance placed in series with the movable coil. The scale is marked in volts, and the resistance is made such that full-scale deflection is obtained when the voltage for which the instrument is designed is impressed across its terminals. Compare the resistance of a millivoltmeter with the resistances of several voltmeters of differ-

A LABORATORY COURSE IN ELECTROCHEMISTRY

ent ranges. Compute the current which flows through each instrument at full-scale deflection. In the double scale voltmeter, the series resistance is divided into two portions, and a third binding post is placed between the resistance coils. What must be the relation between the total resistances of the instrument when using the upper and the lower scales, if one scale is twice the other? Fifty times? Verify your prediction by looking up the resistances marked on laboratory instruments.

The ammeter is made up of a millivoltmeter, and a carefully made resistance called a shunt. The current to be measured is sent through the shunt, and the millivoltmeter is connected so that it reads the fall of potential produced in the shunt by the current. The scale is usually marked directly in amperes. For currents less than 100 amperes, the shunt is often concealed within the case of the instrument, but for very large currents, it is always separate from the millivoltmeter, and is then called an external shunt. It is evident that, by the use of a second shunt having a different resistance, the range of the instrument may be greatly altered.

Danger! The millivoltmeter, usually marked ammeter, designed for use with an external shunt, must never be directly connected to the electrical circuit.

Voltmeters may be protected from injury by taking care to connect them to the circuit so that the deflection of the needle is in the proper direction, and by never connecting them to a source of pressure greater than the scale reading. When in doubt whether a circuit is of high or low pressure, use a high reading instrument.

Ammeters should be protected by a rheostat of such resistance that the current will be within the range of the ammeter. Fuses may of course be used, but they are not necessary for careful students.

The number and range of voltmeters and ammeters

used should be recorded. The use of instruments of ranges unsuited to the experiment may give inaccurate results, or one of the instruments may be at fault. In the latter case, a calibration of the instrument, and the substitution of the correct values will avoid the necessity of repeating the experiment.

The notebook should be about $7 \times 8\frac{1}{2}$ inches, ruled in small squares. Experiments should be numbered and dated, and each should begin at the top of a page, with the title, or a statement of the purpose of the experiment. The original data, and the calculated results should be recorded in a single table. The equation by which the results are calculated should be given, together with a sample substitution of numerical values in the equation. This will assist the instructor in locating mistakes in calculation. Observations made during the experiment may be made below the table, or on the opposite page, but an endeavor should be made to confine the experiment to two pages that face.

Current densities are given in amperes per square decimeter unless otherwise stated.

Laboratory Experiments

The passage of a unidirectional current through an electrolyte is accompanied by the liberation of some substance at each electrode. If the liberated substances are capable of combining with the electrodes under the conditions of the experiment, they do so. If incapable of combining with either the electrodes or the electrolyte, they are set free at the electrodes.

The first seven experiments are qualitative in nature and are intended to give familiarity with the general nature of the process of electrolysis. Each student should perform them all. Their satisfactory perfor-

10 A LABORATORY COURSE IN ELECTROCHEMISTRY

mance requires constant attention and keen use of the eyes to observe all that happens. Phenomena demanding attention are the solubility or insolubility of anodes, the evolution of gas at either or both electrodes, what classes of substances are liberated at the anode and what at the cathode, and the effect of low- and of high-current densities (0.2 to 5 amperes per sq. dm.) The questions with each experiment are intended as suggestions, not as limitations to observation by the student. Litmus paper will prove useful in detecting changes which might otherwise be overlooked. The reactions occurring at the electrodes or in the electrolyte may be expressed most briefly by chemical equations.

EXPERIMENT 1

THE EFFECT OF DIFFERENT ELECTRODES UPON THE PROCESS OF ELECTROLYSIS

Using about an eight percent solution of copper sulphate, connect three cells in series.

ANODE	CATHODE
a. copper	carbon
b. carbon	carbon
c. lead	lead

Pass a current of about 0.5 amperes per sq. dm. and observe the effect upon the electrodes and the electrolyte. Increase the current to three or four times its initial value, and after five minutes again observe the effects. What electrodes are insoluble in this electrolyte? What is the gas?

Similarly use dilute sulphuric acid as electrolyte.

ANODE	CATHODE
d. lead	lead
e. copper	lead

EXPERIMENT 2**REACTIONS BETWEEN ELECTRODE PRODUCTS**

Pass current through three cells in series.

ANODE	CATHODE	ELECTROLYTE
a. lead	lead	NaNO_3 15 percent
b. iron	iron	NaNO_3 15 percent
c. iron	iron	NaCl 15 percent

What anodes are insoluble? Explain the formation of precipitates. Why the different results in *b* and *c*? What are the gases? How do you explain the surprising phenomenon which occurs in *b* at low-current densities? Can current pass without equivalent chemical change?

EXPERIMENT 3**ELECTROLYTIC REDUCTION**

Use a lead anode, and a cathode of galena (PbS) in dilute sulphuric acid. What chemical changes occur?

EXPERIMENT 4**ELECTROLYSIS OF POTASSIUM BROMIDE**

Use an anode of platinum wire, and a cathode of copper in a ten percent solution of potassium bromide. Place the electrodes far apart, and test with litmus paper between as well as at the electrodes. Use a very small current at first. Increase this until there is a change in the action occurring at the anode. Such liberation of gas at anode or cathode may usually be brought about by the use of extremely high-current densities. How do you explain it?

12 A LABORATORY COURSE IN ELECTROCHEMISTRY

EXPERIMENT 5

THE EFFECT OF THE CATHODE MATERIAL UPON ELECTROLYSIS

Electrolyze a ten percent solution of salt, using a very small (0.05 ampere) current for the first three minutes, and the two cells in series.

a. With carbon electrodes.

b. With a carbon anode and a mercury cathode. Pour a thin layer of mercury into the electrolytic cell and make contact with it by means of an insulated wire.

What difference is noted in the two cells on starting electrolysis? Is it a case of the passage of current without chemical change at one electrode? After five minutes, wash the mercury free from the salt solution, place 5 c.c. distilled water on it and set aside in contact with litmus paper. Repeat the experiment with a fresh portion of mercury using a current of about 1 ampere to hasten action.

The mercury cathode is extensively used in commercial cells for the electrolysis of sodium chloride.

EXPERIMENT 6

THE ELECTRO-DEPOSITION OF LEAD

With lead electrodes electrolyze a fifteen percent solution of lead nitrate or lead acetate. Dilute the solution with three volumes of water and repeat.

EXPERIMENT 7

AN EXAMPLE OF THE MAKING OF CHEMICAL COMPOUNDS ELECTROLYTICALLY

In Luckow's patented process for the manufacture of white lead, the electrolyte consists of 13 g. sodium chlorate

and 2 g. sodium carbonate per liter. Carbon dioxide diluted by air is passed in at the cathode.

Use lead electrodes with 0.25 amperes per sq. dm. in this electrolyte, stirring occasionally by hand, or continuously by a jet of air, for a quarter of an hour. The carbon dioxide may be omitted in this brief experiment. Examine the product for pigment purposes.

Now repeat the experiment using as electrolyte a solution of 15 g. sodium carbonate per liter. Look up the solubilities of lead carbonate, lead chlorate and lead hydroxide, if you do not already know them.

What is the use of the sodium chlorate? Since a basic carbonate of lead is the product desired, and sodium carbonate is necessary for its continuous production, is it not strange that so little sodium carbonate is used in the electrolyte. Explain.

The claim is made for this process that the electrolyte is not used up, that white lead can be produced continuously by hanging in lead anodes, blowing in carbon dioxide and passing the current. Can you demonstrate this claim by equations of the various reactions?

Classify as soluble or insoluble the anodes so far used.

Specific Resistance or Resistivity of Electrolytes

In commercial electrolysis it is desirable that the resistance of the electrolytes used be as low as possible, in order to minimize the transformation of electrical energy into heat by the passage of the current through the electrolyte. The energy so transformed is directly proportional to the resistance of the electrolyte, and to the square of the current, and is usually referred to as the I^2R loss. One of the first questions to be answered concerning any electrolyte proposed for commercial electrolysis is, "What is its resistivity?" Resistivities are

14 A LABORATORY COURSE IN ELECTROCHEMISTRY

expressed in ohms per centimeter cube, and may be conveniently determined by readings of current and fall of potential across the electrolyte contained in a vessel of uniform and known cross section and length. It is obviously necessary that the electrodes completely fill the ends of the vessel. Since the resistance of electrolytic conductors is greatly affected by temperature, the thermometer should be read for each determination.

To obtain the total resistance of the solution, apply Ohm's law— $R = \frac{E}{I}$. The resistivity is obtained by dividing the total resistance by the length in centi-

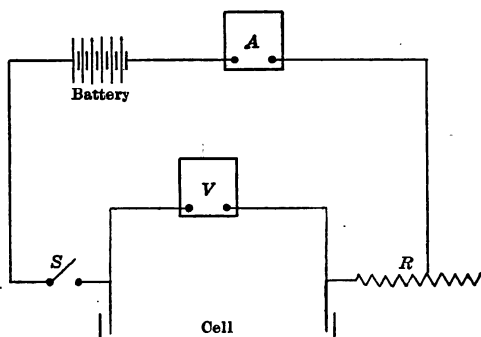


FIG. 1.

meters, and multiplying by the area in square centimeters. Why? A simple way of obtaining the cross section is to measure the volume of electrolyte, and divide this by its length. Polarization may cause serious errors unless special precautions are taken.

In the experiments immediately following, it is desirable for comparison of the resistivities of different electrolytes and of the same electrolyte measured by different methods, that readings be made at some fixed tempera-

ture in all experiments, 25°C. is suggested. It may be of interest to obtain readings at other temperatures also. The continued passage of current will raise the temperature of the electrolyte.

The voltmeter, ammeter, rheostat, switch and electrolytic cell may be connected as shown in Fig. 1.

EXPERIMENT 8

THE RESISTIVITY OF A NORMAL SOLUTION OF COPPER SULPHATE

In a rectangular vessel about 10 cm. long, and 15 to 20 sq. cm. in section, put 120 to 150 c.c. of solution. Use electrodes of clean sheet copper, an ammeter of about 1 ampere capacity, a rheostat and voltmeter suited to whatever low pressure, 5 to 10 volts, may be available. Connect as in Fig. 1. Measure the distance between electrodes. For this experiment secure one reading at a current below 0.1 ampere, and one above 0.5 ampere at the same temperature. Having secured all data desired, replace the copper electrodes by clean sheets of lead and repeat.

Does the voltmeter needle return to zero at once in each case on opening the switch? If not, record the highest reading each time. This is the polarization referred to later.

Compute the total resistance and the resistivity.

Is there any choice as regards accuracy between the use of a current of 0.1 and 0.5 amperes in this experiment?

Polarization

The E.M.F. observed in some cases when the switch is opened is due to polarization. Since there is a complete electrical circuit through the voltmeter, this E.M.F. must

send a current through the electrolytic cell. What is the direction of this current compared to that of the original current when the switch was closed? It is for this reason that the E.M.F. which results from the passage of current through an electrolytic cell is often called the *Counter Electromotive Force of Polarization*. Its cause is the same as that of the E.M.F. of any voltaic cell, which may consist of two unlike electrodes making contact with a single electrolyte, or even of like electrodes in two different electrolytes, i.e., an unsymmetrical electrochemical system. Initially, many electrolytic cells consist of like electrodes in a uniform electrolyte, as in the last experiment. If the passage of current causes polarization, investigation will show that the system has become unsymmetrical by a change in at least one electrode, or a change in the material, concentration, or temperature of the film of electrolyte in contact with the electrode.

In all future experiments where polarization is noted, the student should observe whether it is due to a change in the material of the electrode, or electrolyte, or to a concentration change in the latter. This is important for the attainment of a practical knowledge of electrochemical phenomena.

Correction for Errors Due to Polarization

In calculating the resistance of electrolytes by Ohm's law, it was assumed that the E.M.F. observed was entirely spent in forcing current through the electrolyte, but it is evident that part of it was offset by the counter E.M.F. of polarization, so that the equation should be:

$$R = \frac{E - P}{I}$$

Recalculate the former values of resistivity, correcting

for polarization. What was the percent of error in the uncorrected values?

EXPERIMENT 9

THE RESISTIVITY OF NORMAL COPPER SULPHATE USING A HIGH E.M.F.

Using a cell 30 to 40 cm. long, and 8 sq. cm. in cross section, measure the resistivity of normal copper sulphate and normal sulphuric acid solutions with lead electrodes and a 110-volt source of pressure. Take care that a suitable rheostat is employed and that it is adjusted for its *highest* resistance before closing the switch. An application of Ohm's law will tell whether the rheostat selected is sufficient to reduce the current within the range of the 1 ampere ammeter used. What is the percent of error in resistivity due to polarization?

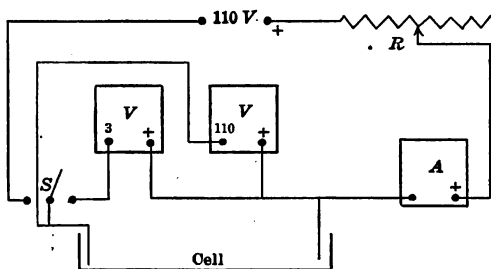


Fig. 2.

If it is desired to read the polarization with greater accuracy than can be done with the high-range voltmeter used, the diagram in Fig. 2 may be employed for connecting another low-reading voltmeter by means of a double-throw switch so that this is not in the circuit until after the line switch has been opened. A double-scale voltmeter may be used instead of two instruments

18 A LABORATORY COURSE IN ELECTROCHEMISTRY

by connecting as in Fig. 3. If the instrument has two positive terminals, as is the case with some makes, they must be connected to the switch and to the anode, instead of to the cathode as shown. This involves transferring the switch to the anode side of the cell.

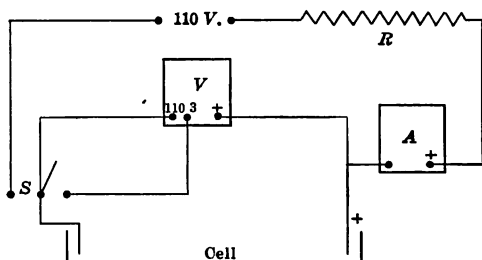


Fig. 3.

EXPERIMENT 10

THE RESISTIVITY OF METALS AND ALLOYS

Measure the resistivity of 3 or 4 feet of fine wire. Between Nos. 22 and 30, copper, iron, monel and nichrome may be used. The current should be small enough to cause no sensible heating. A millivoltmeter may be substituted for the voltmeter in any case where the latter has proved of too high a range. A low-voltage circuit should be used, and since the ordinary rheostats are not of sufficient resistance for use in series, they may be used in shunt, as shown in Fig. 4.

The fullline voltage is impressed across the rheostat, then by the sliding contacts any desired fraction of this is picked off for use. This method is useful whenever it is desired to increase the impressed E.M.F. from zero up by small increments.

Measure the diameter of the wire by a micrometer and compute the resistivity. Determine whether the resis-

tivity increases or diminishes with rise of temperature, by passing a current large enough to heat the wire appreciably; compare the result with the resistivity at the lower temperature. A conductor whose resistance increases with rise of temperature has a positive temperature coefficient of resistance. Do you find that of metals and alloys to be positive or negative? That of electrolytic conductors?

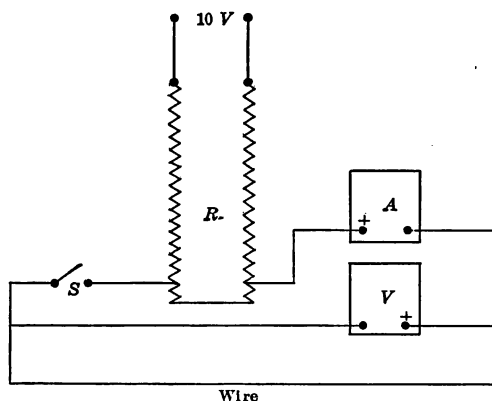


FIG. 4.

EXPERIMENT 11

RESISTIVITY OF ELECTROPLATING SOLUTIONS

Measure the resistivity of several of the following plating solutions, either taken from the laboratory plating tanks, or made up according to the formulas on pages 72-79.

1. Nickel solution.
2. Brass solution—a deadly poison!
3. Copper cyanide solution—a deadly poison!
4. Acid copper sulphate solution.
5. Zinc solution.

Avoid polarization by the use of a soluble anode like the metal deposited, or ascertain its amount (pages 16-18), and correct for it. If soluble electrodes are used, they must be the same as the metal in solution in order that the bath may not be spoiled by the introduction of a foreign metal.

Correction for the Voltmeter Current

A reference to Fig. 1, page 14, will show that the ammeter reads the current flowing through the voltmeter in addition to that passing through the electrolytic cell. Look up the resistance of the voltmeter used in experiment 11, and by applying Ohm's law, compute the voltmeter current for several of your readings. To what extent does this error affect the resistivities previously computed? Is it desirable to apply the correction or not? Why?

This error in the data may be avoided by connecting the voltmeter so that it includes both the cell and the ammeter. Draw a diagram showing this connection. This arrangement should be used in measurements involving currents of a few hundredths of an ampere, or else the correction for the voltmeter current should be applied to the current readings.

EXPERIMENT 12

MEASUREMENT OF THE RESISTANCE OF A VOLT- METER

The resistance of a voltmeter is usually marked upon the instrument by the maker, but this may become obliterated, so that it is sometimes necessary to measure the resistance of a particular voltmeter. If another voltmeter of about the same range and known resistance is

available, the two are connected in series in a suitable circuit, and the readings recorded. Since the fall of potential over different parts of any electrical circuit is proportional to the resistances, it is evident that the resistances of the two instruments are in the same ratio as their respective readings.

Measure the resistances of two voltmeters against that of a standard instrument.

EXPERIMENT 13

THE MEASUREMENT OF RESISTANCES BY USE OF A VOLT-METER ONLY

Resistances may be measured without the use of an ammeter by the connections shown in Fig. 5.

The voltmeter used must, of course, be adapted to the line pressure employed. First throw the S.P.D.T. switch

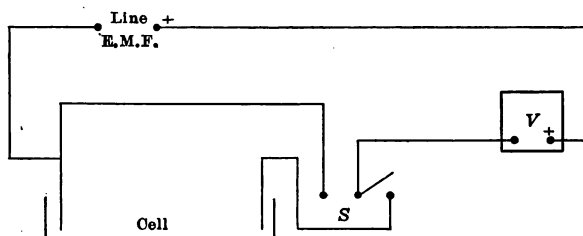


FIG. 5.

"S" to the left, and read the line voltage E , then throw the switch to the right, connecting the cell in series with the voltmeter, and read E' . The resistance of the cell is found from the formula $R = R' \times \frac{E - E'}{E'}$, in which

R' is the resistance of the voltmeter. The principle is that of experiment 12. $E - E'$ is the fall of potential over what?

For respectable accuracy it is necessary that E' lie between $\frac{E}{3}$ and $\frac{2E}{3}$ in value. The length and cross section of the electrolyte may be varied to secure this result. It may even be necessary to change to a voltmeter of higher or lower resistance (probably necessitating a change in line voltage) to secure the above condition. The use of a high E.M.F. lessens the error caused by polarization. Why?

Study this method by measuring the resistivity of

- a. Normal copper sulphate.
- b. $\frac{1}{100}$ normal copper sulphate.
- c. Hydrant water.

EXPERIMENT 14

MEASUREMENT OF RESISTANCE BY USE OF VOLTMETER AND RESISTANCE BOX

If a resistance box is available, the principle of experiment 13 may be more conveniently applied by connecting as in Fig. 6.

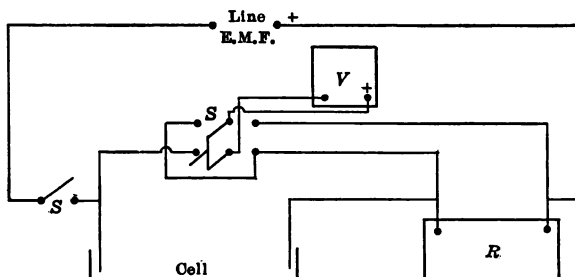


FIG. 6.

S' is a D.P.D.T. switch for connecting the voltmeter successively across the resistance box and the cell. The resistance should be adjusted until the voltmeter reading across each is the same; then the resistance of the cell

equals that of the box, except for the error due to polarization. By opening S when S' is closed to the left, the polarization may be read. Having determined the polarization, it is easy to correct for it. How?

By this method measure the resistivity of a nickel plating bath and of hydrant water. Add one part of the plating solution to twenty-four parts of water, and re-measure. What error is caused in each by polarization when a correction is not applied for it?

EXPERIMENT 15

THE TEMPERATURE COEFFICIENT OF RESISTANCE OF AN ELECTROLYTE

By means of the glass cell shown in Fig 7, measure the resistance of normal copper sulphate between room

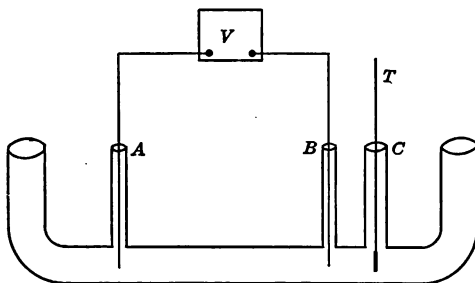


FIG. 7.

temperature and 75° C. taking readings at 10° intervals. Current is sent through the cell by means of copper electrodes, and the fall of potential over a constant length of electrolyte is read on the voltmeter attached to small copper wires introduced through the tubes A and B. Temperatures are read on the thermometer T. A 1-ampere meter and suitable rheostat should be connected in series. Using a 110-volt circuit this particular elec-

24 A LABORATORY COURSE IN ELECTROCHEMISTRY

trolyte will be heated sufficiently by the current. To avoid a rise of temperature while the readings are being made, it is suggested that 0.6 to 0.7 ampere be used for heating, and that this be reduced to 0.2 ampere when it is desired to take a reading. This change may be made conveniently by the use of a double-throw switch. The small lamp rheostats are already provided with this.

If air bubbles are caught in the tube when filling it, what will be their effect upon the results? Why? Watch for the collection of air in the tube at the higher temperatures also. Plot the results in the form of a curve, and determine the temperature coefficient, α , for the intervals 30° to 40° and 60° to 70° , from the formula $R' = R^\circ (1 + \alpha t)$.

F. Kohlrausch's method of measuring the resistance of electrolytes by means of alternating current, using the slide-wire bridge and a telephone receiver, completely eliminates polarization, but has special errors of its own, so that on the average it is but slightly more accurate than the fall-of-potential method. This method is described in Ostwald-Luther's *Physiko-Chemische Messungen*, 2nd edition, pages 395-411.

EXPERIMENT 16

THE EFFECT OF THE SOLVENT UPON RESISTIVITY

Previous experiments have shown that the resistivity of electrolytes varies with the nature of the dissolved substance, and with its amount. The solvent also has a marked effect upon resistivity.

Dissolve 15 g. copper nitrate in 150 c.c. of distilled water, also in the same amount of denatured alcohol. By one of the previous methods measure the resistivity of each solution.

EXPERIMENT 17

RESISTANCE OF A FUSED ELECTROLYTE

Support a small iron crucible with a binding-post attached to it over a Bunsen burner. Make a flat spiral of No. 18 B. & S. gauge iron or nichrome wire, bend the end in the center up at right angles to the spiral and suspend this as one electrode a half inch above the bottom of the crucible. Rigidly support a thermo couple inside the crucible, and connect it to its milli-voltmeter. Connect a double scale 0-15-150 voltmeter

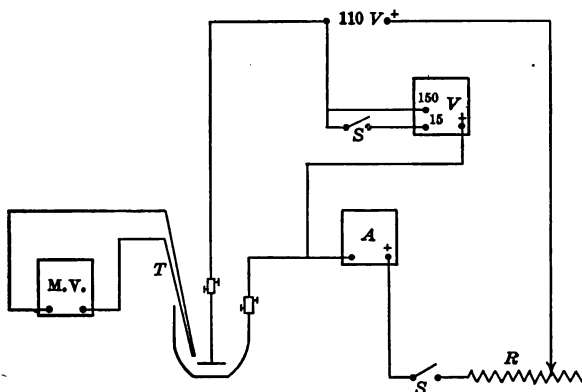


FIG. 8.

across the electrodes, and a low-reading ammeter and a lamp bank in series with the 110-volt circuit as indicated in Fig. 8.

The switch S' which connects the low scale of the voltmeter to the circuit should be closed only at the instant of taking a reading, and then only when the reading on the high scale shows the voltage to be well within the range of the low scale. Put some pulverized sodium nitrate in the crucible, light the burner, and add more

26 A LABORATORY COURSE IN ELECTROCHEMISTRY

sodium nitrate as it melts. When enough is melted, begin taking readings at one minute intervals. Record time, amperes, volts, and millivolts. When heated sufficiently, shut off the gas and take readings as it cools. Solidification should be indicated by a slight lag in the rate of cooling.

Plot the temperature-resistance curve, and note the location of the point of sharpest inflection as compared with the freezing temperature.

Sodium hydroxide may be used in place of the nitrate.

EXPERIMENT 18

THE EFFECT OF HEAT UPON THE INSULATING POWER OF GLASS

Support at both ends over a wing-top burner, a piece of glass rod $1/4$ to $3/8$ inch in diameter. Wind two pieces of No. 20 nichrome wire tightly about the rod at a distance of 1 cm. apart, and connect them to a 110-volt circuit through a low-reading ammeter and a lamp bank. Connect a voltmeter across the electrodes. Heat the rod and wires, read current and pressure and compute the resistivity of the glass. Is there any polarization?

EXPERIMENT 19

THE ELECTROLYSIS OF GLASS AT 300° C.

Prepare about 300 gr. of sodium amalgam by alloying three percent of sodium with warm mercury, or by the electrolysis of a saturated salt solution with a mercury cathode. Place this in a small iron crucible and support in its center a test-tube containing pure mercury. Weigh accurately both the test-tube and the mercury. Connect the crucible as anode and the mercury as cathode with a rheostat, ammeter and voltmeter; heat to 300° C.

(pyrometer) and electrolyze for an hour or more. Before closing the circuit, record the E.M.F. of the cell, and during electrolysis open the circuit from time to time and record the polarization.

Reweigh the mercury and the test-tube, and examine the latter for any sign of corrosion or chemical action. Place 2 to 3 c.c. distilled water on the mercury, together with a piece of red litmus paper. Inference? The ampere-hours passed, multiplied by 0.86 gives the weight of sodium in grams which should have been deposited at 100 percent current efficiency. How does this agree with the gain in weight of the mercury?

The Internal Resistance of Primary and Storage Cells

Let E = the E.M.F. generated by the cell;

Let R = its internal resistance, and

Let R' = the resistance of the rheostat connected in series with the cell, and assume that the resistance of the connecting wires is negligible in comparison, as is usually the case. When the cell delivers the current I

$$E = IR + IR' \text{ or } IR' = E - IR.$$

If now the fall of potential E' across the rheostat be read, and this be substituted above,

$$E' = E - IR \text{ or } R = \frac{E - E'}{I}.$$

The last equation is the one usually employed in measuring the internal resistance of primary and storage cells. Note that for exactness this equation requires that E be the actual E.M.F. generated by the cell when delivering the current I . The value of E is actually found by reading the E.M.F. when the cell is delivering zero current, *i.e.* on open circuit. This open circuit E.M.F. might be taken immediately before or immediately after the current reading. Which will represent more nearly the E.M.F. generated by the cell when the current I flows?

EXPERIMENT 20**THE INTERNAL RESISTANCE OF PRIMARY CELLS**

Measure the internal resistance of a wet cell, also of a new and of an old dry cell. For measuring the resistance of primary cells, it is best to draw only the smallest current which will give a sufficient difference between E and E' to be read accurately on the instrument used. Too large currents cause excessive polarization.

Connect in series with the cell to be tested a switch, a low-reading ammeter, and a rheostat, and connect a voltmeter across the cell terminals. Close the circuit, read the current and E.M.F., open the switch and quickly read E , which is assumed to be the E.M.F. generated by the cell. Obtain data for several values of I , and compute the resistance by the equation given above.

Is it clear that E' is the fall of potential over the rheostat, and not the E.M.F. of the cell itself? If not, consult the laboratory instructor.

Since the voltmeter takes appreciable current when reading the open circuit E.M.F., the assumption that this equals the voltage generated by the cell is incorrect. What percent of the true E.M.F. of the cell is E in the first and last readings?

Another source of error is due to the fact that your values for I include the current through the voltmeter. Compute this current for the two readings just referred to. How serious is this error?

Now correct the first and last values of resistance for both these errors.

EXPERIMENT 21**THE RESISTANCE OF STORAGE CELLS**

Measure the resistance of small storage cells of both the lead and the nickel-iron types. Take care that $E - E'$ is sufficiently large for accuracy.

How do you explain the difference in resistance between the lead cell and the wet primary cell?

EXPERIMENT 22

THE RESISTIVITY OF SODIUM PHOSPHATE

By the fall of potential method using 110 volts pressure, determine the specific resistance of a strong solution of sodium phosphate, first with lead, then with aluminum electrodes.

Is the difference due to polarization? Repeat the measurement using one lead and one aluminum electrode. Now exchange anode and cathode. Keep the cell for the next experiment.

EXPERIMENT 23

ELECTROLYSIS WITH ALTERNATING CURRENT

In a tumbler electrolyze a solution of copper sulphate with carbon electrodes using about 0.5 ampere alternating current. Result? Now put the cell last used in experiment 22 in series in the circuit and pass the same current. Explain.

Faraday's Law

Faraday said, "The chemical decomposing action of a current is constant for a constant quantity of electricity."

The principle has since been variously stated: "The weight of material dissolved or deposited at either electrode is proportional to the current, to the time, and to the chemical equivalent of the substance."

"One gram equivalent of any substance is dissolved, deposited, or decomposed by the passage of 96,540 coulombs (ampere-seconds) of electricity."

For practical application, the most useful form in which to memorize this law is: "For every 26.8 ampere-

hours, 1 gram equivalent of any substance is dissolved, deposited or decomposed."

The current efficiency of all electrolytic processes is determined by a comparison of the product obtained with the yield calculated by the application of this law. In order to do this, it is necessary to measure the quantity of electricity in coulombs, or ampere-hours, and the amount of the desired product formed in the same time. In technical operations, the average current as read on a calibrated ammeter may be multiplied by the time in hours, or the same result may be read directly from the dials of a recording ampere-hour meter. In laboratory experiments involving small currents, it is customary to place in series with the electrolytic cell whose efficiency it is desired to investigate, a coulombmeter as it is now called—formerly known as a voltameter. For measuring large currents, the coulombmeter may be placed in a shunt circuit through which, by the use of suitable resistances, one-half, one-tenth or any desired fraction of the total current is made to pass.

The coulombmeter is an electrolytic cell which obeys Faraday's law, and is so arranged that the gas or metal deposited can be accurately measured or weighed.

While all electrolytic cells obey Faraday's law in the sense that the total amount of material deposited at the cathode by a direct current is strictly in accordance with the law, some of the metal may be dissolved by an acid or other corrosive substance present in the electrolyte, or some other substance may be deposited along with the one desired so that only a portion of the current is usefully employed. In copper refining, the large amount of sulphuric acid in the electrolyte attacks both anode and cathode, with the result that the current efficiency at the cathode is below, and that at the anode is above 100 percent. The coulombmeter has this advantage over the

ammeter; it gives the ampere-hours with fair accuracy in spite of considerable variation of the current and it requires no attention; while with an ammeter, the current must be kept constant by varying the resistance, or the variations in current must be recorded, which necessitates watching.

The silver coulombmeter is the world's standard by means of which the value of the ampere is fixed. For ordinary laboratory use, however, the cheaper and less troublesome copper coulombmeter is sufficiently accurate.

EXPERIMENT 24

THE CONSTRUCTION OF A COPPER COULOMBMETER

Oettel, *Practical Exercises in Electrochemistry*, pp. 16, 22. The electrolyte should consist of 150 g. of copper sulphate, 50 g. of sulphuric acid, 50 g. of alcohol and 1 liter of water. A rectangular battery jar makes a good container. Two anodes of heavy sheet copper should be cut with projections for hanging them on the top of the jar. The single cathode of thin sheet copper should be accurately weighed. For tests of several hours' duration, the electrolyte should be stirred by a jet of hydrogen, or a mechanical stirrer. With good circulation, 3 amperes per sq. dm. of cathode surface may be used. At the end of the test, wash the cathode with distilled water, rinse with alcohol and dry quickly over a flame. Oettel gives 1.182 g. of copper deposited per ampere-hour, corresponding to a current efficiency of 99.58 percent.

EXPERIMENT 25

THE ELECTROLYSIS OF WATER MADE CONDUCTIVE BY SODIUM HYDROXIDE

Fill the graduated glass apparatus for the decomposition of water with a ten percent solution of purest sodium

32 A LABORATORY COURSE IN ELECTROCHEMISTRY

hydroxide, and connect in series with it a rheostat, an accurate ammeter of low range and a small copper coulombmeter made as above. Current should be passed for a few minutes to saturate the solution with the gases before any gas is collected for measurement. Hold the current constant during the test by adjusting the rheostat, which must be capable of very fine adjustment. Calculate the ampere-hours from the weight of copper deposited, and determine the current efficiency of hydrogen and oxygen production, and the error of the ammeter. The necessary constants for hydrogen and oxygen follow.

	HYDROGEN	OXYGEN
1 liter gas at 0° and 760 mm.		
weighs.....	0.089873 g.	1.42900 g.
1 ampere-hour liberates.....	0.03759 g.	0.2983 g.

To read the volume of gases collected, adjust the level of liquid in the open tube to that in the gas tube, read the volume and temperature of each gas, and the height of the barometer in millimeters. To obtain the pressure under which the gas was measured, subtract from the height of the barometer the tension of aqueous vapor at the temperature of the gas. Change the gas temperature from centigrade to the absolute scale by adding 273. The gas volume may be reduced to the standard, 0° C. and 760 mm. by use of this equation

$$V^{\circ} = V' \times \frac{273}{\text{absol. temp.}} \times \frac{\text{pressure}}{760}.$$

State the two gas laws involved in the above equation; also that involved in the subtraction of the tension of aqueous vapor from the height of the barometer. Is an error introduced by the fact that the gases are measured over a solution of caustic soda instead of over pure water?

EXPERIMENT 26**THE ELECTROLYSIS OF WATER MADE CONDUCTIVE BY
SODIUM NITRATE**

Using the decomposing cell of the previous experiment in series with an accurate ammeter, electrolyze a ten percent solution of sodium nitrate until an amount of gas suitable for measuring has been collected. Compute the current efficiency as before. Explain the results.

Potential and Electromotive Force

When any conductor of the first class (metallic conductor) is dipped into a conductor of the second class (electrolytic conductor) a difference of potential results. A different first-class conductor gives a different potential. If, then, two different metals be simultaneously immersed in the same electrolyte, there should be a difference of potential between the metals. In other words, the arrangement constitutes a voltaic cell.

EXPERIMENT 27**MEASUREMENT OF THE ELECTROMOTIVE FORCE BETWEEN
CONDUCTORS OF THE FIRST CLASS**

Prepare clean sheets (3×5 inches) of the following materials: iron, zinc, copper, lead, brass, aluminum, carbon and lead peroxide. The last may be a strip cut from the positive plate of an old storage cell, and freshly formed by using it as anode in dilute sulphuric acid for eight to ten hours.

Using a voltmeter having a range of 3 or 5 volts, measure the E.M.F. between copper and the other materials in a ten percent solution of sodium sulphate, noting in each case which electrode is attached to the

positive terminal of the voltmeter. To avoid injury to the voltmeter by an E.M.F. in the wrong direction, first test the direction of E.M.F. in each combination by barely touching for an instant the tip of the electrode to the solution.

Arrange the electrodes in the order of their potentials, calling the lowest zero, and assigning a numerical value to each of the others. From your measurements should copper be called electro-positive to zinc, or vice versa? The current entered the voltmeter at the positive terminal; in which direction, then, did it flow through the voltaic cell?

Also measure the potential of the other electrodes against lead peroxide, and arrange a similar series with lead peroxide as zero. Compare the values of a combination of the same two electrodes in each series.

During measurements, note changes of E.M.F. due to polarization at one electrode.

Single Potentials

Further measurements would bring out even more clearly the additive nature of the E.M.F. of voltaic cells, that the E.M.F. is the sum of the potentials of the separate electrodes.

It is evident that, if the potential of some particular electrode be chosen as the standard or zero, by measuring the E.M.F. between this and other electrodes, a scale of electrode potentials can be arranged similar to our thermometer scales of temperature differences. This has been done, and the situation in regard to potential scales in use today is strikingly like that of the thermometer scales. We have three thermometer scales in use, two of them with different zero points, and all of them requiring negative values to indicate the range of

temperatures encountered in the world. There are two full potential scales in use, and measurements are occasionally made in terms of other incomplete scales, used only for special purposes. The potential scales are also like our temperature scales in that they require negative values to express the potentials of many substances.

The student should particularly observe that a negative value for the single potential does not, of itself, denote anything unusual or distinctive about that metal, but that the negative sign results from the arbitrary location of the zero at a particular place in the scale. Had the zero been located at the bottom, all potentials would have been positive; and if at the top, all potentials would be negative, yet the order of the series, and the physical, chemical and electrochemical properties of the electrodes would remain absolutely unchanged.

Several of the standard electrodes referred to have been used for the purpose of following the changes in potential occurring at the plates of the lead storage cell during discharge and charge. The zinc electrode formerly used for this purpose has now been superseded by cadmium, on account of its more constant potential and less rapid corrosion by the battery acid. A lead peroxide electrode has also proved satisfactory for this purpose, if allowed to stand twenty hours after forming before it is used. The method of using these is to connect one terminal of the voltmeter to the standard electrode and the other to that plate of the cell whose potential is desired. Polarization caused by the voltmeter current is negligible in this case, for the cadmium is always anode so that the only effect of the voltmeter current is to dissolve the cadmium at the rate of 15 or 20 milligrams per hour. Since the composition of the electrode and the electrolyte in contact with it remain practically

unchanged, the potential is constant. The plates of even a small storage cell expose an enormous surface to the electrolyte so that the trifling amount of hydrogen liberated on them by the voltmeter current does not affect their potential appreciably. (For a discussion of Polarization, see page 15.)

With the small electrodes which it is frequently necessary to use in the laboratory, the use of a voltmeter causes a considerable change in the potential at one or both electrodes. For measuring accurately the E.M.F. between small electrodes, the potentiometer described on page 37 is far more satisfactory than the voltmeter.

The Normal Calomel Electrode

The standard of potential most generally used is the normal calomel electrode. A convenient form of this consists of a wide mouth bottle of 120 c.c. capacity, with a layer of mercury 1 cm. deep in the bottom, on which is the same depth of mercurous chloride, previously washed with normal potassium chloride solution and shaken with mercury to remove any mercuric chloride. The bottle is nearly filled with normal potassium chloride solution. Connection with the mercury is made by a platinum wire sealed in the tip of a glass tube containing a little mercury, from which a copper wire makes contact with the external circuit. Connection with the electrolytic cell, the electrode of which it is desired to test, is made by means of potassium chloride solution contained in a glass tube which makes contact with the main body of solution in the calomel electrode. To this glass tube is attached a short rubber tube ending in another glass tube bent at right angles and drawn down to a small point. A plug of filter paper or asbestos is fitted tightly into the end of

the glass tube to hinder diffusion of solutions into the normal electrode. The bottle should be closed hermetically (Why?) by a three-hole rubber stopper, the third hole of which carries a small dropping funnel filled with normal potassium chloride solution, by means of which the plug of filter paper is washed out after use.

This electrode has several features to recommend it. The materials are cheap and readily obtainable, it is easily constructed and does not polarize (change potential) with the passage of a minute current in either direction. The student should explain its freedom from polarization by considering the chemical changes which occur when the mercury is anode, and when cathode. See page 39 for precautions in its use.

The value -0.56 volt has been assigned to its potential. The scale of electrode potentials constructed with this as a basis resembles the Fahrenheit scale of temperatures in that no constant of nature happens to coincide with zero of the scale.

On account of the high resistance of the calomel electrode, a voltmeter cannot be used for measuring the E.M.F. between this and other electrodes. For this purpose a potentiometer is required.

A Simple Potentiometer and its Use

A two-dial rheostat consisting of nine 100-ohm coils, and ten 10-ohm coils makes a cheap and satisfactory potentiometer. Connections should be made to $x - y$, the points whose E.M.F. is to be measured, as shown in Fig. 9.

The middle posts, C, D, of the potentiometer, to which the sliding arms are attached, are to be connected in series with the short-circuit key K, the galvanometer G, and the points $x - y$. A source of E.M.F. indicated at

B, and slightly greater than that to be measured, is connected across the outer terminals E, F, of the potentiometer. One or two good dry cells will serve for this purpose and their E.M.F. should be measured from time to time during use by an accurate voltmeter. Instead of using a voltmeter, the unknown E.M.F. may be compared with a standard cell by connecting the latter across one end of a D.P.D.T. switch, the circuit

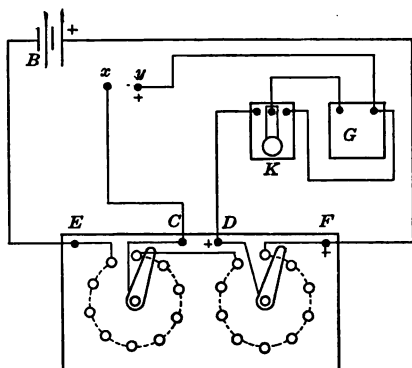


FIG. 9.

$x - y$, G, K, across the other end, and the binding posts C, D, to the blades of the switch.

The unknown E.M.F. must be connected so that it opposes B as shown in the diagram. The dials are adjusted until the galvanometer indicates no current, when the unknown E.M.F. at $x - y$ equals the fall of potential between D and C. The value of this is obtained by multiplying the E.M.F. of B by the reading of the potentiometer expressed as thousandths. The third decimal place is obtained from the swings to the right and left of the galvanometer needle as one of the 10-ohm coils is introduced and cut out between C and D.

EXPERIMENT 28

THE EFFECT OF THE MATERIAL OF THE ELECTRODE UPON
POTENTIAL

In a normal solution of sodium or potassium sulphate, measure the E.M.F. between the normal calomel electrode and electrodes of cadmium, carbon, copper, iron, lead, lead peroxide, silver, tin and zinc.

Connect the calomel electrode at y and the metal at x. When so connected, *i.e.* the wire from the calomel electrode leading to the positive terminal of the potentiometer, the reading should be marked positive, but if it is found necessary to change the calomel to the negative side in order to secure a balance, the potentiometer reading should be marked negative. This change is most conveniently made by a pole-reversing switch in the battery circuit, by which the polarity of the potentiometer is reversed, leaving the galvanometer circuit undisturbed. A convenient tabular form of record follows:

Electrode	Potentiometer reading	Battery E.M.F.	Cell E.M.F.	Electrode potential
Nickel ...				

In case the E.M.F. varies with time, this variation should be recorded.

Compute the electrode potential by multiplying the potentiometer reading by the E.M.F. impressed across its terminals. The product is the E.M.F. of the cell consisting of the metal and the calomel electrode. To this add algebraically the potential of the calomel electrode (-0.56) and the result is the potential of the metallic electrode.

40 A LABORATORY COURSE IN ELECTROCHEMISTRY

Form an electrochemical series by arranging the electrodes in the order of their potentials.

EXPERIMENT 29

THE EFFECT OF THE COMPOSITION OF THE ELECTROLYTE UPON POTENTIAL

Measure the potential of the same electrodes in a tenth normal solution of potassium cyanide, and compare the results with those obtained in the last experiment.

EXPERIMENT 30

THE EFFECT UPON POTENTIAL OF CONCENTRATION OF THE ELECTROLYTE

Measure the potentials of copper, iron, and zinc in a saturated solution of salt, and in the same diluted to a tenth, a hundredth, and a five-hundredth of the original concentration.

EXPERIMENT 31

THE EFFECT OF TEMPERATURE UPON ELECTRODE POTENTIAL

Measure the potentials of copper, iron, and zinc in a ten percent salt solution at room temperature, at about 0°C. , and at 100°C.

EXPERIMENT 32

THE EFFECT OF DISSOLVED AIR UPON ELECTRODE POTENTIAL

Measure the potential of platinum, copper and zinc in a ten percent salt solution at atmospheric pressure, then exhaust the air by means of the laboratory filter pump, taking readings of time and potential.

For doing this, put the electrolyte into a bottle similar to the calomel electrode. Drill a very small hole through

a two-hole rubber stopper, through it pass a number 14 or 16 copper wire so that it fits air tight, and attach the metal electrode to this. Insert the tube of the calomel electrode in one hole, and in the other put a glass tube connected to one leg of a glass Y tube. Remove the dropping funnel from the calomel electrode, and insert in its place a glass tube connected to the other leg of the Y tube, and connect the Y tube to the filter pump.

May not the potential of the calomel electrode change as a result of removing the air from its electrolyte, and so mask any change at the other electrode? Test this by comparing its potential with another calomel electrode before and immediately after exhausting the air. How prevent re-absorption of air by the calomel electrode before its potential can be measured?

EXPERIMENT 33

THE EFFECT OF GASES OTHER THAN AIR UPON ELECTRODE POTENTIALS

Measure the potentials of copper, zinc and platinum in a ten percent salt solution, then pass in a stream of illuminating gas, hydrogen or CO_2 , and continue reading.

The Polarization of Voltaic Cells

The polarization of a voltaic cell may be readily investigated by the use of the calomel electrode.

EXPERIMENT 34

THE POLARIZATION OF A SIMPLE VOLTAIC CELL

Hang sheets of amalgamated zinc and of copper in five percent sulphuric acid and connect them through a switch, ammeter and a resistance of 5 to 10 ohms. Connect a voltmeter of about 1500 ohms resistance across the plates, and set up a calomel electrode to read the potential

of the copper plate. Read E.M.F. and potential, then close the switch, and take readings at intervals of two to three minutes. What is the cause of the change?

PRECAUTION. In order to avoid including the IR drop through the electrolyte in the potential reading, the tip of the calomel electrode should be placed as close to the copper as possible, and behind the electrode, *i.e.* out of the line of current flow. The other alternative is to open the switch a fraction of a second before depressing the key of the galvanometer. Test both methods.

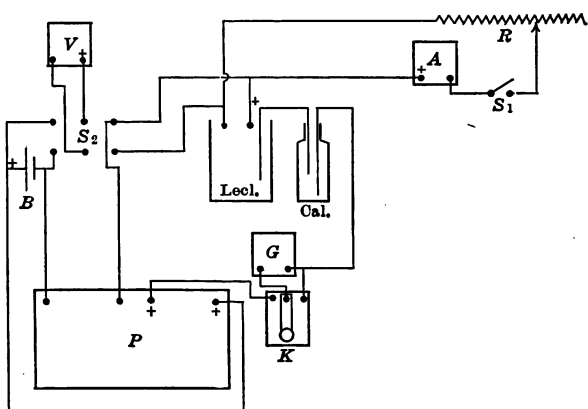


FIG. 10.

EXPERIMENT 35

POLARIZATION IN A LECLANCHE TYPE WET CELL

Connect the cell in series with a rheostat, ammeter and switch, put the tube of the calomel electrode into the electrolyte of the cell and connect with the potentiometer circuit as in Fig. 10.

Connect a voltmeter (3 volt range) to the blades of a D. P. D. T. switch, and connect one end of the switch to the wet cell, the other to the single dry cell which ener-

gizes the potentiometer, so that all E.M.Fs. may be read on the same instrument. Read the open E.M.F. of the cell and the potential of its cathode. Close the switch S, adjust the rheostat for 1 ampere current, and read E.M.F. and potential at five-minute intervals.

Electromotive Force of Decomposition

Experiments 1 to 7 consisted of a qualitative study of some of the chemical changes which occur in electrolysis. It is now proposed to study another phase of electrolysis, viz., the relation between current and impressed E.M.F. as the latter is gradually increased in magnitude.

EXPERIMENT 36

THE E.M.F. OF DECOMPOSITION OF SODIUM CHLORIDE

The apparatus required consists of a voltmeter, (range 5 to 6 volts) an ammeter (range 1 ampere) a

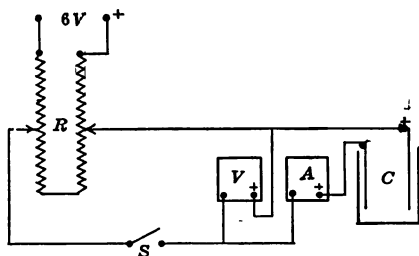


FIG. 11.

slide-wire rheostat of 150 to 200 ohms resistance, a switch, and two carbon or graphite plates of 8 to 10 square inches area.

Place the carbon electrodes in a ten percent salt solution, connect the fixed terminals of the rheostat to a 6- or 10-volt circuit, and by means of the sliding contact transfer to the electrodes increasing fractions of the

44 A LABORATORY COURSE IN ELECTROCHEMISTRY

fall of potential over the rheostat. The voltmeter should be connected as in Fig. 11, so that the current traversing it is not registered by the ammeter.

Do not close the switch until ready to record data. Adjust the rheostat to give the least possible E.M.F. across the cell, and read the E.M.F. and current. Increase the E.M.F. by 0.2-volt intervals until the limit of the voltmeter or ammeter is reached, reading the current corresponding to each E.M.F. Does the current correspond to that calculated from Ohm's law? Using values of E.M.F. as abscissæ and of current as ordinates, plot the current-E.M.F. curve.

The results are characteristic of electrolysis with insoluble electrodes. The E.M.F. at which the current rises suddenly is called the E.M.F. of decomposition. What is its value in this case? Some have attempted to fix upon a definite value by extending the straight part of the curve backward until it cuts the E.M.F. axis, calling the point of intersection the E.M.F. of decomposition. Draw such a line to your curve.

EXPERIMENT 37

THE COUNTER E.M.F. OF POLARIZATION

Why does Ohm's law not apply to the relation of current to E.M.F. in the last experiment? To learn this, repeat the experiment opening the switch after reading the current at each value of E.M.F., and as quickly as possible read the counter E.M.F. of polarization. Plot the current-E.M.F. curve as before, and on the same sheet plot the polarization-E.M.F. curve, marking values of polarization as ordinates on the right margin of the sheet.

Why does an impressed E.M.F. of one volt produce no current, while at three volts current passes? Follow

the polarization curve, comparing the polarization with the E.M.F. at several points. Is their relation a constant one throughout the curve? Has it any causal connection with the current curve?

Measurement of the Polarization at Anode and Cathode

We have seen that the passage of current through an electrolytic cell may develop a counter E.M.F. of con-

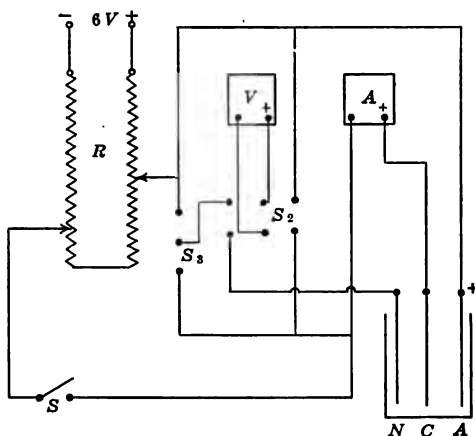


FIG. 12.

siderable magnitude. It is of interest to learn whether only one, or both electrodes contribute to this E.M.F. This may be learned by introducing a metal plate which is not connected to the electrolyzing circuit, and measuring the E.M.F. between this and each of the active electrodes at the outset, and for each value of the polarization. The connections are given in Fig. 12.

S_2 is a D. P. D. T. switch, S_3 a S. P. D. T. switch, R a slide-wire rheostat, A the anode, C the cathode, and N

the reference electrode. To read the total polarization throw S_2 to the right and then open the line switch S for an instant. For the E.M.F. between N and the cathode throw S_2 to the left and S_3 down; for the anode throw S_3 up while S_2 is thrown to the left. By comparing the E.M.F. between each electrode and the standard during electrolysis, with its initial value, the polarization (change of potential caused by the passage of current) may be determined. Note that in voltaic cells the positive terminal of the voltmeter is always attached to the cathode; therefore the other electrode is the more electro-positive of the two.

EXPERIMENT 38

THE E.M.F. OF DECOMPOSITION AND ANODE AND CATHODE POLARIZATION FOR ZINC BROMIDE

In the above manner, determine the E.M.F. of decomposition, the total polarization, and the polarization at each electrode, using carbon electrodes in a solution of zinc bromide, with a sheet of zinc 5×3 inches, scoured with pumice, as the reference electrode.

It will be noted that with increase of impressed E.M.F. the anode becomes more and more electro-negative, while the cathode becomes less so.

Plot the current-E.M.F. curve with values of current at the right, and the three polarization curves (total, anode and cathode) with values of polarization at the left. The zero of polarization should be placed sufficiently high so that all negative values for anode polarization fall upon the sheet.

Instead of zinc, carbon might have been used as a reference electrode. This would be advantageous in that the polarization of each electrode could be read directly, but the carbon is more likely to change its potential during the experiment than the zinc. Why?

EXPERIMENT 39**THE E.M.F. OF DECOMPOSITION OF SULPHURIC ACID
AND THE POLARIZATION OF LEAD ELECTRODES**

By the method of the previous experiment, determine the E.M.F. of decomposition, total polarization, and the polarization at anode and cathode, using lead electrodes in normal sulphuric acid. The reference electrode may be lead peroxide or roughened sheet lead. The former has the advantage of greater constancy. If used, it should be prepared as follows: Charge a strip from the positive plate of a lead storage cell as anode for six to ten hours, until oxygen is vigorously evolved, then use as cathode at a low current for twenty minutes, and allow to stand over night in dilute sulphuric acid before use. A piece of the negative plate from a storage cell, charged as cathode, makes a good substitute for a sheet lead reference electrode. Plot curves as in experiment 37.

E.M.F. of Decomposition by Observation with a Lens

Another method of determining the E.M.F. of decomposition is by using as electrodes platinum wires, sealed into glass tubes with 5 to 6 mm. exposed, watching with a lens for the first product of decomposition appearing at either electrode. A voltmeter is connected across the electrodes to measure the E.M.F. applied, which should be very gradually increased until decomposition is attained. The E.M.F. may be controlled as shown in Fig. 12. Several trials are usually necessary to find the minimum pressure at which decomposition occurs.

EXPERIMENT 40**THE E.M.F. OF DECOMPOSITION BY OBSERVATION**

By the above method determine the E.M.F. of decomposition of normal sulphuric acid, of a normal solution

of copper sulphate, and of fifteen percent nitric acid. Do products appear simultaneously at both electrodes in every case? If not, continue to raise the pressure until deposition occurs at the other electrode. Decomposition must have occurred when the first product was liberated; why then did not the product appear at the other electrode also?

The use of the voltmeter for measuring potentials requires electrodes of several square inches area in order to prevent serious alterations of potential by the current required to operate the voltmeter. Platinum electrodes of this size are often unavailable, in which case the potentiometer should be substituted for the voltmeter.

EXPERIMENT 41

THE MEASUREMENT OF POLARIZATION BY USE OF THE POTENTIOMETER

With platinum electrodes, a potentiometer and milliammeter, determine the decomposition and the counter E.M.F. of polarization of normal hydrochloric acid, hundredth normal hydrochloric acid, fifteen percent nitric acid, and normal sulphuric acid.

Connect as in Fig. 11 (page 43) except that the potentiometer (Fig. 9) is substituted for the voltmeter, and the negative terminal of the latter is changed to the other side of the switch. Why? For each value of E.M.F. read the current, then open the switch and instantly tap the galvanometer key. If a special combined switch-and-key (described on page 52) is available, the interval between opening the switch and closing the galvanometer circuit may be shortened. Note the E.M.F. at which products of decomposition are evolved at the electrodes.

Plot the current-E.M.F. and polarization-E.M.F. curves as usual. Compare the E.M.F. of decomposition of sulphuric acid with the value obtained in experiments 39 and 40. Compare your results with Le Blanc's values in Table 11 page 144.

The theory of electrolytic dissociation postulates that the molecules of electrolytes are decomposed by the mere act of dissolving; it might therefore be expected that the only E.M.F. required to send current through electrolytes would be that due to the ohmic resistance, and that conduction in all electrolytes would at all times obey Ohm's law. How do you reconcile the theory of electrolytic dissociation with your experiments? In this connection, try the experiment which follows.

EXPERIMENT 42

DETERMINATION OF THE E.M.F. OF DECOMPOSITION OF NORMAL COPPER SULPHATE WITH COPPER ELECTRODES

This may be carried out either with large electrodes and the voltmeter after the manner of experiment 36, or with small electrodes and the potentiometer as in experiment 41.

EXPERIMENT 43

THE EFFECT OF INEQUALITY IN SIZE OF ELECTRODES UPON E.M.F. OF DECOMPOSITION

Using platinum electrodes, one not over a centimeter square, and the other a decimeter square, determine the E.M.F. of decomposition and polarization of normal sulphuric acid by the method of experiment 41. Note the lowest E.M.F. at which gas appears at either electrode. Explain.

Further Study of the Polarization of Electrodes and Its Relation to the Process of Electrolysis

References:

- Richards and Landis, *Trans. Amer. Electrochem. Soc.*, Vol. 4, pp. 119-125.
 Watts, *Trans. Amer. Electrochem. Soc.*, Vol. 19, pp. 91-106.
 Hitchcock, *Trans. Amer. Electrochem. Soc.*, Vol. 25.
 Leffeldt, *Electrochemistry*, p. 173.

EXPERIMENT 44

E.M.F. OF DECOMPOSITION AND POLARIZATION AT THE ELECTRODES BY THE POTENTIOMETER

With electrodes 1 or 2 cm. square, a voltmeter, milliammeter, potentiometer and calomel electrode, study the electrolysis of the following solutions:

- a. Normal sulphuric acid with platinum electrodes.
- b. Normal hydrochloric acid with platinum electrodes.
- c. Hundredth normal hydrochloric acid platinum electrodes.
- d. Fifteen percent nitric acid.
- e. Ten percent zinc bromide with silver electrodes.
- f. Ten percent zinc bromide with silver cathode and platinum anode.

If possible, carry current up to 200 to 400 milliamperes.

- a. Compare values with those obtained in experiment 39, and explain the differences. With the maximum E.M.F. at the end of the experiment, open the line switch and follow the rate of diminution of polarization at the electrodes by readings at two-minute intervals for ten to fifteen minutes.
- b. and c. Why the difference in curves of anode polarization? Compare the cathode curve with that in a.
- d. Why does not hydrogen from nitric acid produce the

same cathode polarization as hydrogen from sulphuric acid in *a*?

- e.* When maximum polarization is attained, open the line switch S_6 and follow the rate of depolarization as

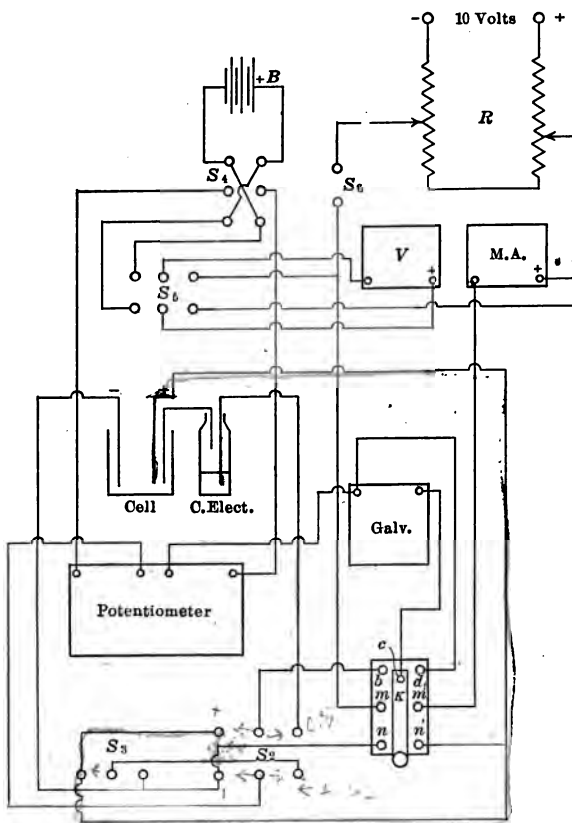


FIG. 13.

directed in *a*. Explain the different rates of depolarization observed in *a* and *c*.
The electrical connections are shown in Fig. 13.

Although this looks complicated, it is easily understood by observing that it consists of four distinct circuits:

1. The electrolyzing circuit comprising a source of E.M.F., a line switch S_6 , a rheostat R , milliammeter MA , switch-key K , and electrolytic cell.

2. The potentiometer circuit, consisting of battery B , reversing switch S_4 , potentiometer, key K , galvanometer, cell, and switch S_2 .

3. Switches S_2 and S_3 for substituting in the potentiometer circuit the calomel electrode in place of either anode or cathode.

4. Switch S_5 by which either the E.M.F. of the electrolytic cell or of the battery B may be read on the voltmeter.

The key K is a combination of a short-circuit galvanometer key (binding posts b, c, d) and a double-pole line switch (binding posts mn and $m'n'$) operated by a single lever. Normally the line circuit is closed, the galvanometer is short-circuited, and the potentiometer circuit is open. On depressing the key, the line is opened and then the potentiometer circuit is closed.

It may require three hours to set up the apparatus. Once set up, it should be left in position for use by other members of the class.

A convenient tabulation for data and results follows:

			Potentiometer readings			Volts, polarization			
E.M.F.	Mil-amp.	E.M.F. of battery	Total	Cathode	Anode	Total	Cathode	Anode	Diff.
0.0	0	4.169	.010	-.100	-.090	.042	-.977	-.935	.042
0.2	0	4.169	.050	-.100	-.150	.208	-.977	-1.185	.208

The line switch S_6 must not be closed until after taking one set of readings to find the initial potential of each

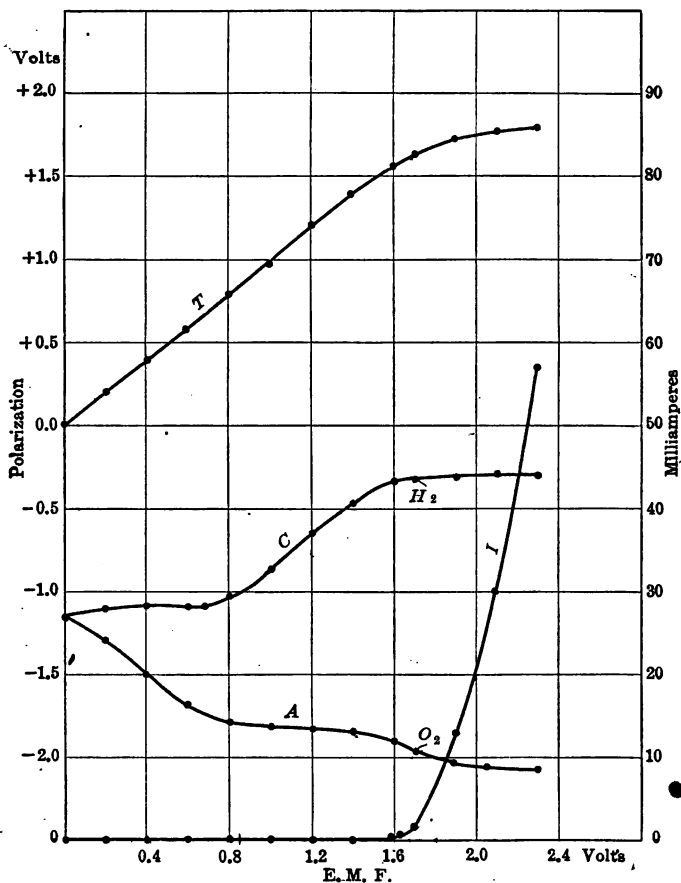


FIG. 14.

electrode. Increase the impressed E.M.F. by steps of 0.2 volts. Note the first appearance of gas at each electrode, and watch the behavior of the milliammeter for any infor-

mation which this may give in regard to the nature of electrolysis. A comparison of the difference between

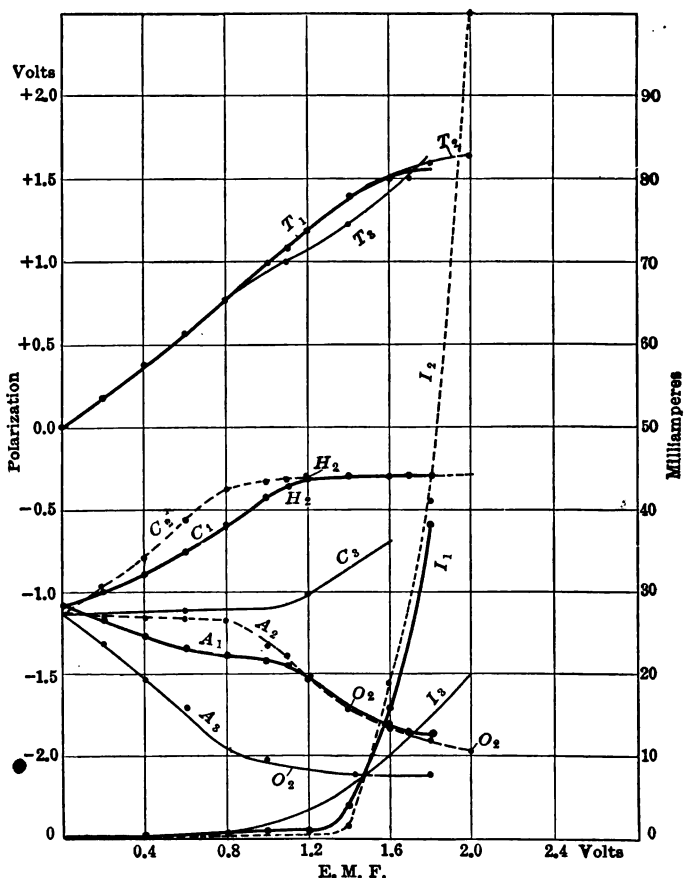


FIG. 15.

anode and cathode potentials with the total polarization gives a check on the accuracy of the measurements.

For computing the polarization from the potentiometer readings, see page 38.

Plot curves of current, and polarization vs. E.M.F. as indicated in Fig. 14, which shows the electrolysis of normal sulphuric acid with platinum electrodes 1 cm. square, placed 1 cm. apart.

In your experiments does the polarization of a platinum cathode by hydrogen follow the same curve in different electrolytes? Explain. What have the various hydrogen-on-platinum curves in common?

Further light on the nature of electrolysis may be obtained by the use of electrodes of unequal size. Fig. 15 shows three separate experiments with platinum electrodes, one of 1 cm., the other of a hundred square centimeters area, a centimeter apart in normal sulphuric acid.

Not only is the polarization at anode and cathode dependent on the relative size of the electrodes, but the total polarization curve T , and the current curve I are also considerably modified.

Experiment 1 was made with a cathode 1 cm. square, and an anode a hundred times as large. The first point of interest is that hydrogen is evolved at an E.M.F. of 1.1 volts, which is 0.6 volts below the usual value for the decomposition of water, although the curve for the total polarization is as usual. Note that anode and cathode polarize about equally up to the point at which hydrogen is first evolved, and that beyond this the polarization of the anode increases rapidly.

Before starting experiment 2, the electrodes were removed from the cell, rinsed, and heated to redness to expel any gases that might have been absorbed by the platinum. They were then returned to the same electrolyte. Although there was a difference of potential of 1.57 volts between the electrodes when they were re-

moved at the end of experiment 1, they are seen to be at the same potential when returned at the beginning of experiment 2, which was merely a repetition of No. 1. The results of this, so far as the polarization of the separate electrodes is concerned, are quite different from the first trial. The polarization of the cathode increases much more rapidly than before, while the potential of the anode remains almost unchanged up to an impressed E.M.F. of 0.8 volts. Other experiments have shown that solutions which have stood long enough to become saturated with air have a marked depolarizing action on the cathode, and prevents its potential from rising as it would do if the dissolved oxygen were not present.

In experiment 3 the smaller electrode is used as anode, and the larger as cathode in a fresh lot of the original solution which, of course, contained dissolved air. The result is that the potential of the large cathode remains practically unchanged up to an impressed E.M.F. of 1.2 volts, when oxygen is evolved at the anode. Beyond this the cathode potential rises rapidly. Notice that hydrogen was obtained in only two of the three experiments. Study the curves and predict what E.M.F. would have been required for the evolution of hydrogen in experiment 3. The current rose steadily beyond 0.8 volts E.M.F. Explain this difference from No. 1 and No. 2. The curves of total polarization in No. 1 and No. 2 coincide. That for No. 3 coincides with the others for only half its length. Why not throughout?

Discharge Potentials

The potential which an electrode must attain in order that a particular substance shall be evolved or deposited upon it has been termed the discharge potential of that substance.

Examine all cathode curves or tabulated data of previous experiments for the first evolution of hydrogen. Prepare a table by recording from each experiment the cathode material, E.M.F., current density in amperes per sq. dm., and the polarization. What seems to be the determining factor in the evolution of hydrogen, the electrolyte, the E.M.F., or the current density?

EXPERIMENT 45

THE DISCHARGE POTENTIAL OF HYDROGEN ON PLATINUM

Using the potentiometer and small cathodes of platinum, copper, mercury and carbon, determine with the aid of a lens the lowest potential for the appearance of hydrogen upon the cathode, also for its escape as bubbles, in solutions of tenth normal sulphuric acid and tenth normal hydrochloric acid.

EXPERIMENT 46

THE DISCHARGE POTENTIAL OF HYDROGEN ON SEVERAL METALS

With cathodes of platinum, nickel and iron determine the same in tenth normal solutions of sodium hydroxide, potassium sulphate and sodium chloride.

EXPERIMENT 47

THE DISCHARGE POTENTIAL OF CHLORINE

By a similar method the discharge potentials of oxygen, chlorine and bromine may be found for insoluble anodes. Determine the discharge potential of chlorine with platinum electrodes in tenth normal solutions of hydrochloric acid and sodium chloride. After the latter determination, electrolyze for ten minutes with a brisk evolution of gas and the formation of some sodium hypochlorite, and repeat the determination. Explain the changed result.

Overvoltage

In experiments 45 and 46 it was seen that the discharge potential of hydrogen varied with cathodes of different materials. The discharge of hydrogen has been found to take place upon platinized platinum at a lower potential than on any other metal. The difference in volts between the discharge potential of hydrogen on platinized platinum and on any other metal is called the overvoltage of hydrogen on that metal. The overvoltage of oxygen at insoluble anodes has also been investigated, but less completely than that of hydrogen. Overvoltage is an important factor in determining the corrosion of metals, the reducing power of different cathodes, and the oxidizing power of anodes.

EXPERIMENT 48

THE OVERTVOLTAGE OF HYDROGEN

In tenth normal solutions of sulphuric acid and sodium chloride, measure the discharge potential of hydrogen on lead, cadmium and tin and find the overvoltage of hydrogen on these metals by comparison with the discharge potential on platinized platinum. With the aid of a lens, find the lowest potential for the permanent clinging of bubbles of hydrogen to the electrode.

Rise of potential with increase in current density varies with different cathodes. Also find the potential for a current density of 1 ampere per sq. dm. Potential readings should be made on open circuit.

The Passive State of Metals an Electrochemical Phenomenon

When iron is immersed in fuming nitric acid, it is for a time rendered immune to attack by dilute nitric or

sulphuric acid. Several other metals may similarly be rendered passive or inert to chemicals which ordinarily attack them. The discovery of the passive state of metals is usually attributed to Schoenbein in 1836, but instances of passivity were observed at much earlier dates. In the Philosophical Transactions for 1790, page 374, Bergman notes that silver dissolved in strong red nitric acid is not precipitated by iron. In the same year Kier found iron dipped in fuming nitric acid insoluble in the same acid of ordinary strength.

EXPERIMENT 49

THE PASSIVE STATE OF IRON

- a. Dip small strips of cleaned sheet iron, or wire nails freed from grease, into dilute solutions of silver nitrate and copper nitrate.
- b. Immerse clean iron in fuming nitric acid, remove and at once dip into the above silver and copper solutions.
- c. Measure the potential of cleaned iron in fuming nitric acid, interposing a small vessel containing sodium or potassium nitrate solution between the nitric acid and the calomel electrode to keep the acid from the latter. It is sometimes said that iron is ennobled by dipping in fuming nitric acid; can you justify this statement?

EXPERIMENT 50

THE PASSIVITY OF IRON ANODES IN CERTAIN ELECTROLYTES

By grinding or pickling, remove the scale from two strips of sheet iron, rinse, and use as electrodes in a ten percent solution of sodium or potassium nitrate contain-

ing a few drops of concentrated nitric acid. Connect in the circuit a low-range ammeter, a voltmeter, and a calomel electrode. Arranged to read the potential of the sheet which is to become anode. How should the voltmeter be connected? Before closing the line switch, determine the potential of the anode. Close the switch, read E.M.F., current, and polarization as the E.M.F. is increased by intervals of 0.25 volts. Compute the current density for each value of current.

EXPERIMENT 51

PASSIVITY VS. POTENTIAL

In strong solutions of potassium chlorate (faintly acidified by nitric acid) and of potassium dichromate, measure the potentials of iron and cadmium anodes at current densities of zero, about 0.5 and 1 ampere per sq. dm.

EXPERIMENT 52

THE PASSIVE STATE MAY SOMETIMES BE UTILIZED IN REMOVING A COATING OF ONE METAL FROM ANOTHER²

Number and weigh accurately several cleaned strips of sheet iron. Electroplate one with copper, another with brass, and a third with nickel. Weigh again. Connect these as anodes with iron cathodes in three cells in series, with an electrolyte consisting of sodium nitrate, a small amount of sodium or potassium nitrite and a little nitric acid. Pass 2 amperes for ten to fifteen minutes. Re-weigh. What is the cause of the exception?

The Corrosion of Metals

For over a half century the corrosion of metals has received much attention from chemists, engineers and

²A Practical Utilization of the Passive State of Metals, C. F. Burgess, Trans. Am. Electrochem. Soc., Vol. 4, pages 31-36.

technical men in general. In later years the corrosion and preservation of steel has become a subject of vast economic importance. It is now generally admitted that electrolysis and voltaic action play an important part in the corrosion of iron, other metals and alloys.

References:

- The Corrosion of Iron and Steel—J. N. Friend.
Corrosion and Preservation of Iron and Steel—Cushman and Gardner.
The Corrosion of Iron from the Electrochemical Standpoint—C. F. Burgess, Trans. Am. Electrochem. Soc., Vol. 21, pages 17-54.
Effect of Substances on Corrosion of Iron by Sulphuric Acid—O. P. Watts, Trans. Am. Electrochem. Soc., Vol. 21, pages 337-353.

EXPERIMENT 53

THE EFFECT OF CONTACT WITH OTHER METALS ON THE CORROSION OF IRON

Clean a sheet of iron, cut it into strips 1×10 cm., number, and weigh them. To each strip fasten in the form of the letter V, one of the following: carbon, copper, lead, tin and zinc (scour the metals with pumice first), and place the combinations inverted in vessels containing a ten percent solution of ammonium chloride. Leave several days until there is marked corrosion of some of the strips. Note time, remove, clean off rust, (see page 90) and weigh. Explain results.

EXPERIMENT 54

THE EFFECT OF CERTAIN SALTS ON THE CORROSION OF IRON BY SULPHURIC ACID

Dilute one volume of concentrated sulphuric acid by 20 volumes of water, put 200 c.c. into each of a number of

62 A LABORATORY COURSE IN ELECTROCHEMISTRY

tumblers, place them in a thermostat at 30° C or some other convenient temperature, and cover by a watch glass. To one add a drop or two of a solution of platinum chloride; to another, 1 g. sodium arsenate; to others, 1 g. copper sulphate, 1 g. tin chloride, 1 g. cadmium sulphate, 1 g. silver nitrate, and to one make no addition.

Clean, number and weigh strips of rather heavy sheet iron 3×3 cm. and put one in each tumbler. At the end of twenty-four hours or more, remove the strips, brush clean, dry and weigh. How do you account for the various results?

EXPERIMENT 55

ACCELERATED CORROSION

It is sometimes desirable to hasten the corrosion of a metal, in which case the principle illustrated in the last two experiments may be utilized.

Prepare dilute sodium amalgam by electrolyzing a strong salt solution in a broad shallow dish with a mercury cathode and a platinum or carbon anode. Divide the amalgam between three tumblers half filled with distilled water. Into one drop a few pieces of chromium, into another drop a carbon rod. Guess at the relative rates of corrosion of the sodium in the three cases.

By arranging to collect the hydrogen in graduated apparatus, an exact determination of the rates may be made. Try the effect of a few drops of acid in the third cell.

How would iron, copper or zinc, act in place of the chromium? What are the qualifications of a satisfactory material for this purpose? What may be the effect of metallic impurities in the mercury of commercial cells for the electrolysis of salt?

EXPERIMENT 56

EFFICIENCY OF THE DEPOSITION OF ALKALI METALS
FROM VARIOUS SOLUTIONS

Operate three cells in series with equal weights of mercury as cathode, with electrolytes of three normal solutions of sodium and potassium chlorides and sodium sulphate. Use anodes of platinum or carbon in the first two, and platinum or lead in the last. Electrolyze an hour with occasional stirring of the mercury. Wash the amalgam quickly, decompose in equal volumes of distilled water by the use of chromium, and titrate the the alkali formed. What was the strength of amalgam? The current efficiency? What reasons can you give for the different results?

The Electrolytic Separation of Metals

When two metals are in the same solution, it is often possible to pass an electric current through the solution under such conditions that only one metal will be deposited, thus effecting a separation of the two.

The more important factors contributing to the success or failure of this process are:

1. The relative position of the two metals in the series of single potentials. If the metals are far apart, they can probably be separated, but if of about the same potential, both deposit together, though there is a tendency for the metal of lower potential to be deposited first.

2. The nature of the electrolyte often determines success or failure. For example, in sulphate solutions the potentials of zinc and copper differ by a volt, and separation is easy, but in cyanide solution their potentials are about the same, and an alloy is deposited.

3. The acidity, alkalinity or neutrality of the electrolyte is important. Acidity is especially so, if the potential of hydrogen lies between the potentials of the two metals which it is desired to separate. The addition of acid then renders separation more certain. In alkaline solutions, the magnitude and relative order of the potentials of several of the common metals are greatly changed.

4. The current density at the cathode affects the result, even when there is a sufficient difference of potential between the two metals to render a separation probable. So long as there is enough of the metal of lower potential in actual contact with the cathode to carry all the current, that metal alone is deposited. If, however, metal is being deposited faster than diffusion can supply it, enough of the second metal will be deposited to make up for the lack of the first metal, unless hydrogen comes between the two, in which case that may be deposited instead of the second metal.

5. Circulation. The function of circulation is to assist diffusion in maintaining in contact with the cathode a sufficient amount of the first metal to carry all the current.

6. Concentration of the electrolyte. It is evident from 4 and 5 that current density, circulation and concentration are interdependent factors—that any change in one of these permits, or makes necessary, a change in one of the others.

It should be noted that some metals, *e.g.* lead, manganese and cobalt may be deposited partly or wholly at the anode as oxides.

For the experiments immediately following, prepare five percent solutions of the sulphates of copper, iron, nickel and zinc.

EXPERIMENT 57

DEPOSITION FROM AN ELECTROLYTE CONTAINING SEVERAL METALS

Fill a tumbler one-fourth full with the solution of ferrous sulphate. With an iron anode and a brass cathode, electrolyze at 1 ampere per sq. dm. Result? Add an equal volume of the solution of zinc sulphate and continue electrolysis. Result? Add the original volume of copper sulphate and continue. Result?

EXPERIMENT 58

DEPOSITION FROM ACID ELECTROLYTES

In three separate vessels put solutions of the sulphates of copper, iron, and zinc, with anodes of the metal in solution, and brass cathodes; electrolyze in series. Add concentrated sulphuric acid to each, drop by drop, with stirring, up to five percent. Note the results from time to time. Finally put in new cathodes, or reverse the original one, to bring a clean portion of it into the electrolyte.

With the aid of tables of electrode potentials, supplemented by your own experiments, explain the results obtained in experiments 57-58.

EXPERIMENT 59

DEPOSITION OF AN ALLOY OF NICKEL AND COPPER

With a nickel anode and a copper cathode, electrolyze the solution of nickel ammonium sulphate. Then add half as much of the copper sulphate solution and continue. Result? To half the above mixture add ammonia until most of the precipitate re-dissolves, then add a solution of potassium cyanide until the blue color disappears. Electrolyze. Result? Explain.

EXPERIMENT 60**THE DEPOSITION OF BRASS**

Mix equal volumes of two percent zinc sulphate and two percent copper sulphate solutions. Electrolyze with brass anode and a lead cathode. Result? Now slowly add dry sodium carbonate with stirring, until evolution of carbon dioxide ceases, then add a solution of potassium cyanide—(deadly poison)—until the blue color disappears and the precipitate is almost, but not quite, dissolved. Electrolyze again. Explain.

Electrolytic Analysis

Chemical analysis by the electrolytic method is now developed to such an extent that it cannot be adequately treated in a book on general electrochemistry. For information on this subject, the student should consult

E. F. Smith—Electro Analysis.

Neumann-Kershaw—Electrolytic Methods of Analysis.

Classen-Boltwood—Analysis by Electrolysis.

One of the greatest improvements in this method of analysis is the shortening of the time from the ten or twelve hours formerly required to fifteen or thirty minutes.

It is evident that any method for the rapid deposition of metals must provide for vigorous circulation in order to bring every atom of metal in contact with the cathode in the limited time allowed for the process. A description of various forms of apparatus suitable for rapid electrolysis may be found in the 5th edition of Smith's Electro Analysis pages 39–67. Since 1909 the author has used a cheap and convenient arrangement, consisting of a cylinder of platinum gauze 5 cm. in diameter and

4 cm. high, weighing with the two conducting wires 9 g., and a motor-driven centrifugal pump of hard rubber with a platinum wire anode wound spirally about it. The strip of gauze used as cathode is 16×4 cm., 7.75 meshes per sq. cm., wire 0.116 mm. diam. (50 meshes per square inch, wire 0.004 inches diam.) Its actual sur-

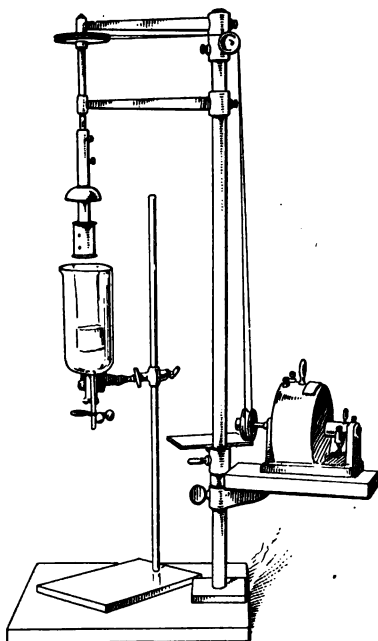


FIG. 16.

face, calculated by the formula $S = 2\pi dlb\sqrt{n}$, in which l = length of gauze, b = breadth and n = number of meshes per sq. cm., is 13 sq. cm. The maximum current is fixed by the carrying capacity of the conducting wires. A recent modification consists in substituting a gauze anode for the wire. The electrolyzing vessel may

be a tall type beaker, or an inverted bottle with the bottom removed and a tube passing through the rubber stopper for drawing off the electrolyte. The cathode should be held centered by a frame of light glass rod. The stirring is very effective, since there is circulation from top to bottom as well as rotation of the electrolyte, and the jets thrown by the pump pass directly through the gauze cathode. The apparatus is shown in Fig. 16.

EXPERIMENT 61

THE ELECTROLYTIC DETERMINATION OF COPPER

Weigh accurately about 1 g. of c. p. copper sulphate, dissolve it in 150 c.c. of warm distilled water, add five drops of strong nitric acid and electrolyze in the apparatus just described. Test for complete precipitation by drawing out 1 c.c. of the solution, making alkaline by ammonia then acidifying by acetic acid, and adding a few drops of a solution of potassium ferrocyanide. A brownish color or precipitate indicates the presence of copper. After precipitation is complete, without interrupting the current, displace the electrolyte by water so that the copper shall not be attacked by the free acid present; or the cathode may be removed very quickly after interrupting the current, plunged into water, rinsed with distilled water, then with absolute alcohol, and dried by hot air.

Note the E.M.F., current, time required, speed of rotation and appearance of the deposit. Too large a current will produce a dark or spongy deposit. Make one or two check analyses.

EXPERIMENT 62

THE ELECTROLYTIC DETERMINATION OF NICKEL

Dissolve about 1 g. of pulverized nickel ammonium sulphate, or 0.7 g. nickel sulphate in 120 c.c. of water,

add 4 g. ammonium sulphate and 30 c.c. of strong ammonia. Electrolyze as above. Test for complete precipitation by adding a solution of hydrogen sulphide to 1 c.c. of the electrolyte. A brown color indicates nickel. The nickel must be entirely removed from the platinum by the use of warm sulphuric or nitric acid.

Some Electrochemical Puzzles

EXPERIMENT 63

INTERMEDIATE ELECTRODES

Electrodes which carry current without metallic connection with the external circuit are called intermediate electrodes.

In each end of an oblong rectangular glass vessel 5 or 6 inches long, place a small carbon electrode and between these suspend horizontally a carbon rod or platinum wire 2 1/2–3 inches long, with its ends toward the electrodes. Fill the cell with an eight percent solution of potassium bromide (or sodium chloride). Is the carbon rod a better or a poorer conductor than the electrolyte beside it? Predict how current will flow through the central part of the cell where it has a choice of passing by electrolytic or metallic conduction.

Connect a voltmeter to the terminal electrodes, apply an E.M.F. increasing by increments of 0.25 volt, and note results. Explain.

EXPERIMENT 64

A ROTATING INTERMEDIATE ELECTRODE

(W. D. Bancroft, Trans. Am. Electrochem. Soc., Vol. 7, p. 171)

Across the middle of a rectangular glass jar fit a vertical partition consisting of a pine board 1 inch thick.

Boil this in melted paraffine until well impregnated. In the middle of the top bore a 1 1/4 inch hole to a depth of 4 inches, and fix a pivot in the bottom of the hole. Drill a hole in one end of a graphite rod (1 inch diam.) to fit the pivot, fix another bearing at the upper end, and cut a groove near the top to carry a twine belt, so that the rod can be rotated about a vertical axis by a motor. This leaves the graphite rod exposed to the electrolyte on each side of the board diaphragm.

Fill the cell with a solution of 100 g. copper sulphate and about 10 g. sulphuric acid per liter, put electrodes of sheet copper in the ends of the cell, and connect an ammeter (range 1 ampere), a voltmeter, and a rheostat as in Fig. 11, page 43.

Obtain data for current-E.M.F. curves, first with the graphite rod stationary, then when it is revolving. Try different speeds of revolution. Explain.

EXPERIMENT 65

ALUMINUM ELECTRODES

Insert weighed aluminum electrodes in a gas coulombmeter, fill it with fifteen percent aluminum chloride solution, and with an accurate ammeter, electrolyze, at about 0.2 ampere. Collect, measure, and identify the gas at each electrode. Determine the current efficiency for metal and gas at each electrode. Explain the anomaly.

Electroplating

The following books on electroplating should be available for consultation by students:

- Barclay and Hainsworth—Electroplating.
- Field—Principles of Electro-deposition.
- Langbein-Brannet—Electro-deposition.

Watt-Philip—Electroplating and refining.
Trans. Amer. Electrochemical Soc., Vol. 23.

“The Brass World” and “The Metal Industry” contain many articles concerning commercial electroplating, and the questions and answers in each issue reflect troubles and current practice.

Students are advised to read the following articles:

1. Composition of Electroplating Solutions—Keith, Trans. A. E. S., 3, 227-44
2. Chemistry of Electroplating—Bancroft, Tr. A. E. S., 6, 27-43.
3. Physical Character of Metal Deposits—Burgess and Hambuechen, E. and M. I. 1, 204-7.
4. Physical Characteristics of Electro-deposited Metals—Johnson, E. & M. I., 1, 212-4.
5. Alloying of Metals as a Factor in Electroplating—Kahlenberg, E. & M. I., 1, 201-2.
6. Tests on Elliptical Anodes—Burgess and Hambuechen, E. & M. I., 1, 347-8.
7. Adhesion of Electrolytic Metal Deposits—Burgess and Hambuechen, J. Phys. Chem., 7, 409-15.
8. Electro-deposition of Nickel—Kern and Fabyan, School of Mines Quarterly, 29, 342-70.
9. Deposition of Nickel—Johnson, Tr. A. E. S., 3, 255-9.
10. Efficiency of the Nickel Plating Tank—Brown, Tr. A. E. S., 4, 83-99.
11. Injurious Effect of Acid Pickles on Steel—Burgess, E. & M. I., 4, 7-11.
12. Phenomena of Metal Depositing—Betts, Tr. A. E. S., 8, 63-79.
13. Function of Addition Agents in Electrolytes—Kern, Tr. A. E. S., 15, 441-74.
14. Electro-deposition of Lead from Perchlorate Baths—Mathers, Tr. A. E. S., 17, 261-72.
15. Unsolved Problems in Electroplating—Hogaboom, Tr. A. E. S., 19, 53-9.
16. A Modern Electroplating Plant—M. & Ch. E., 8, 274-5.

The Composition of Plating Solutions

A collection of the various solutions that have been proposed for the electro-deposition of the more common metals may be found in several papers published in Vol. 23 of the Transactions of the American Electrochemical Society. A perusal of these papers will suggest many interesting experiments.

The composition of the following plating solutions is stated in grams of solids for 1 liter of water. Current densities are given in amperes per sq. dm., and resistivities in ohms per centimeter cube.

1. Brass Bath—Roseleur's, from Pfanhauser's *Elektroplattirung*.

Sodium carbonate, dry, Na_2CO_3	10 g.
Cupric acetate, pulv. $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot$	
H_2O	14 g.
Sodium bisulphite, NaHSO_3	14 g.
Zinc chloride, fused, ZnCl_2	14 g.
Potassium cyanide, 100 percent, KCN	40 g.
Ammonium chloride, NH_4Cl	2 g.

Current density 0.3 ampere. E.M.F. 2.7 volts. Resistivity 13.6. Specific gravity 1.0545 ($7\frac{1}{2}^\circ$ B $\acute{\text{e}}$). Current yield sixty-five percent. Deposit in one hour, 0.0041 mm.

Prepare the solution by dissolving the sodium salts in 400 c.c. of warm water, stir the copper and zinc salts with 200 c.c. of water and slowly stir this into the first solution. Dissolve the cyanide in the remainder of the water, and stir into the other portion of the bath, when the precipitate should dissolve. Add the ammonium chloride and boil for an hour, replacing the water evaporated.

2. Copper Bath, Acid.

Copper Sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	200 g.
Sulphuric acid, conc. H_2SO_4	30 g.

Current density 1 to 3 amperes. Resistivity 9.3. Specific gravity 1.1417 (18°Bé). Current yield 100 percent.

3. Copper Bath, Alkaline.

Sodium sulphite, Na_2SO_3	20 g.
Sodium carbonate, cryst., $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	20 g.
Sodium bisulphite, NaHSO_3	20 g.
Cupric acetate, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$	20 g.
Potassium cyanide, 100 percent KCN	20 g.

Current density 0.3 amperes. E.M.F. 2.9 volts. Resistivity 14.3. Specific gravity 1.0507 (7°Bé). Current yield seventy-one percent. Deposit in one hour 0.0056 mm. Temperature 20°C . Make up as directed under bath No. 1.

4. Gold Bath for regular gilding on all metals.

Sodium carbonate, dry Na_2CO_3	10 g.
Gold (as double chloride of gold and ammonium) $(\text{NH}_4)_2 \text{AuCl}_6$	2 g.
Potassium cyanide, KCN	7 g.

Current density 0.1 amperes. E.M.F. 2.8 volts. Resistivity 44. Specific gravity 1.0175 ($2 \frac{1}{2}^\circ \text{Bé}$). Current yield ninety-nine percent. Deposit in one hour, 0.00184 mm. Temperature 20°C . Anodes of gold one-third the area of the cathode.

5. Gold Bath for hot gilding of articles that are to be only partly covered with gold. Cyanide attacks enamel or lacquer.

74 A LABORATORY COURSE IN ELECTROCHEMISTRY

Potassium ferrocyanide, $K_4Fe(CN)_6$	15 g.
Sodium carbonate, dry Na_2CO_3	15 g.
Gold chloride, $AuCl_3$	2.65 g.

Current density 0.1. E.M.F. 2.1 volts. Resistivity 18.3. Specific gravity 1.0247 (3 1/2° B $\acute{e}$). Current yield ninety-five percent. Deposit in one hour 0.00123 mm. Since gold anodes are insoluble, carbon anodes may be used. Temperature 50° C.

6. Iron Bath.

Ferrous sulphate, $FeSO_4 \cdot 7H_2O$	150 g.
Ferrous chloride, $FeCl_2 \cdot 4H_2O$	75 g.
Ammonium sulphate, $(NH_4)_2SO_4$	100 g.

Current density 1 ampere. This bath is suitable for refining iron and yields good deposits an inch thick. At 20° C. the deposit is hard and brittle, but electrolysis at 80°–90° yields a softer metal.

7. Lead Bath for refining.

Lead (as $PbSiF_6$)	50 g. to 80 g.
Hydrofluorsilicic acid, H_2SiF_6	100 g. to 150 g.
Gelatine	0.5 g.

Current density 1.2 to 1.6 amperes. For plating, the amount of free acid may be diminished to two or three percent.

8. Nickel Bath for iron and steel.

Nickel ammonium sulphate, $Ni(NH_4)_2$ $(SO_4)_2 \cdot 6H_2O$	75 g.
--	-------

Current density 0.3 ampere. E.M.F. 3.5 volts. Resistivity 24.6. Specific gravity 1.0479 (6 1/2° B $\acute{e}$). Current yield 91.5 percent. Deposit in one hour, 0.0034 mm. Cast anodes should be half the area of cathode.

9. Nickel Bath for brass and copper, not for iron.

Nickel sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	50 g.
Ammonium chloride, NH_4Cl	25 g.

Current density 0.5 ampere. E.M.F. 2.3 volts. Resistivity 17.6. Specific gravity 1.0357 (5°Bé). Current yield 95.5 percent. Deposit in one hour, 0.0059 mm. Cast anodes should be half the area of the cathode.

10. Nickel Bath for pointed objects and for the direct nickeling of zinc.

Nickel sulphate	40 g.
Sodium citrate	35 g.

Current density 0.27 ampere. E.M.F. 3.6 volts. Resistivity 51.7. Specific gravity 1.0394 ($51/2^\circ \text{Bé}$). Current yield ninety percent. Deposit in one hour 0.00301 mm. Rolled anodes should have two and a half times the area of the cathode.

11. Nickel Bath for thick deposits.

Nickel sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	50 g.
Ammonium tartrate (neutral), $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$	36 g.
Tannin	0.25 g.

Current density 0.3 ampere.

12. Black Nickel.

Nickel ammonium sulphate	60 g.
Ammonium sulphocyanide	15 g.
Zinc sulphate, cryst.	7 g.

Use nickel anodes three to four times the surface of the cathode. Current density 0.05. E.M.F. 0.5 volt. The deposit takes on any metal which can be nickeled, but is best over white nickel. The full black is obtained only on polished metal. The solution must be kept

strictly neutral by addition of nickel carbonate, as acid makes the deposit gray or streaky, and alkali causes brittleness and flaking off.

13. Platinum Bath—Roseleur's.

	For thin Deposits Pfanhauser	For Thick Deposits
Ammonium phosphate	20 g.	100 g.
Sodium phosphate	100 g.	100 g.
Platinum, as platinum chloride	2.3 g.	10 g.

Current density 1 to 2 amperes, E.M.F. 3 to 4 volts.

Dissolve the platinum chloride in 100 c.c. of water. Dissolve the ammonium phosphate in 200 c.c. of water and add to the solution of platinum chloride. Dissolve the sodium phosphate in 700 c.c. of water and stir it into the platinum solution, when the precipitate previously formed will dissolve. Boil until the odor of ammonia has disappeared and add water to make up for evaporation. The bath should have an acid reaction, and should be used hot.

14. Platinum Bath—Böttger's.

Citric acid	105 g.
Caustic soda to neutralize	
Ammonium platinic chloride from 1.58 g. PtCl_4	

Dissolve the citric acid in 400 c.c. of water, neutralize by caustic soda, and to the boiling solution add the ammonium platinic chloride formed by dissolving the platinum chloride in a small amount of water and precipitating it by 0.5 g. of ammonium chloride dissolved in a few c.c. of water. Make up to 1 liter with water.

15. Silver Bath—for heavy plating.

Silver as silver cyanide	25 g.
Potassium cyanide	27 g.

Current density 0.3 ampere. E.M.F. 1.3 volts. Resistivity 28.8. Specific gravity 1.0338 (4 3/4 Be). Current yield ninety-nine percent. Deposit in one hour 0.0114 mm. Area of anodes equals area of cathode.

16. Silver Bath—for ordinary plating.

Silver as silver chloride	10 g.
Potassium cyanide, 100 percent	20 g.

Current density 0.3. E.M.F. 1.5 volts. Resistivity 35. Specific gravity 1.0175 (2 1/2 B $\acute{e}$). Current yield 100 percent. Deposit in one hour 0.0115 mm.

17. Silver Striking Solution.

Silver as silver cyanide	4 g.
Potassium cyanide	100 g.

18. Brightener for Silver Bath.

Carbon bisulphide, CS ₂	45 g. or 35.5. c.c.
Regular silver bath	1000 c.c.

Shake thoroughly and allow to stand twenty-four hours before use. Some advise adding a volume of ether equal to the carbon bisulphide. For use, add 0.7 c.c. of the above to each liter of the silver bath. This may best be done by putting the proper amount of brightener in a large bottle, adding a liter or two of the silver bath and shaking until a uniform solution is obtained. This is to be thoroughly stirred into the bath in the plating tank. Larger amounts of brightener give a dull deposit, and an excess spoils the deposit.

19. Amalgamating Solution or Quick Dip.

Mercuric oxide (red)	6 g.
Potassium cyanide	100 g.

20. Tin Bath—Roseleur's.Sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$ 40 g.Tin chloride (fused), SnCl_2 16 g.Tin chloride (cryst.), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 4 g.

Current density 0.3 ampere. E.M.F. 2 volts. Resistivity 40.2 Specific gravity 1.0357 (5° Bé). Current yield ninety-nine percent. Deposit in one hour 0.0059 mm. Anode area equal to cathode. This solution may be used for direct deposition on copper, brass, bronze or zinc; but iron or steel must be coppered first or given a preliminary coat of tin by an immersion bath. The tin anodes do not corrode satisfactorily and tin salts must be added occasionally to maintain a sufficient amount of tin in solution.

21. Tin Baths.

	a	b	c
Caustic soda, NaOH	90 g.	120 g.	125 g.
Tin chloride, cryst. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	30 g.	30 g.	50 g.
Sodium hyposulphite, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	15 g.	60 g.	75 g.
Sodium chloride, NaCl	15 g.		

Use hot or cold with anodes of pure tin.

22. Tin Bath—for contact tinning:

Cream of tartar, $\text{KHC}_4\text{H}_4\text{O}_6$, saturated solution	1000 c.c.
Tin chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	20 g.

Small objects of copper or brass may be given a thin coating by boiling in this bath in contact with pieces of granulated tin.

23. Tin Bath—for tinning iron by immersion.

Ammonium alum, $(\text{NH}_4)_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$	25 g.
Tin chloride, fused, SnCl_2	2 g.

A bright coating is produced on clean iron by 30 to 60 seconds immersion in the boiling solution.

24. Zinc Bath.

Zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	100 g.
Ammonium chloride, NH_4Cl	25 g.
Ammonium citrate, $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$	40 g.

Current density 0.5 to 1.0. E.M.F. 1.1. to 2.2. Resistivity 15.9. Specific gravity 1.0781 (10 1/2° B $\acute{\text{e}}$). Current yield 100 percent. Deposit per ampere-hour 0.0173 mm.

25. Zinc Bath :—(Metal Industry, 1906, 85).

Zinc chloride	60 g.
Ammonium chloride	30 g.
Hydrochloric acid	4 g.
Glycerine	4 g.

Use anodes of zinc and of antimonial lead in equal numbers. The bath remains clear and gives a fine white deposit. (Addition of ammonium sulphate would assist in protecting the lead from corrosion.)

26. Zinc Bath—Hansen-Van Winkle Co.

Zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	150 g.
Aluminum sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	50 g.
Sulphuric acid	1 g.

Coloring and Oxidizing Metals

A few of the many formulæ for the production of various colors on metals are given below.

27. Black on Brass.

Ammonia, conc.	160 c.c.
Water	160 c.c.
Sodium carbonate, dry	10 g.

Copper carbonate freshly precipitated until excess remains undissolved. Heat to 70° C. and immerse the brass only until the desired color is obtained. The color is made more permanent by immersion in a hot ten percent solution of caustic soda.

28. Bright Black on Brass.

Muriatic acid, HCl	800 c.c.
White arsenic, As_2O_3	200 g.
Antimony chloride, SbCl_3	120 g.

This works best hot, and no water should be added. Dip the brass repeatedly until the desired color is obtained. The color will stand light scratch-brushing. The addition of 100 g. of ferrous sulphate gives a bluish black. The solution is said to work best electrolytically with steel anodes.

29. Olive Green on Solid Brass.

Copper sulphate	80 g.
Ammonium chloride	20 g.
Water	1000 c.c.

Boil the objects in this solution.

30. Antique Green on Brass.

Nickel ammonium sulphate	60 g.
Sodium hyposulphite, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	60 g.
Water	1000 c.c.

Heat to 70° C. and dip the objects. It gives a dark, slaty green.

31. Antique Green on Brass or Copper.

Acetic acid	100 g.
Ammonium chloride	30 g.
Sodium chloride	10 g.
Cream of tartar	10 g.
Copper acetate	10 g.

Add a little water and smear over the brass. Allow to dry for twenty-four to forty-eight hours, and relieve the high lights with a brush touched to beeswax.

32. Hardware Green on Brass.

Ferric nitrate $\text{Fe}(\text{NO}_3)_3$	8 g.
Sodium hyposulphite	45 g.
Water	1000 c.c.

Heat to 70°C . and immerse the object a few seconds.

33. Brown on Solid Brass or Copper.

Potassium chlorate, KClO_3	40 g.
Nickel sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	20 g.
Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	180 g.
Water	1000 c.c.

Dip the article in pure boiling water, then boil in the above solution, rinse, dry and buff with a fine brush.

34. Brilliant Blue on Brass or Copper.

Lead acetate	15 g.
Sodium hyposulphite	25 g.
Water	1000 c.c.

Heat to 80°C ., immerse the cleaned object for two to twenty seconds, rinse, dry, and lacquer. The color fades after several months.

35. Brown to Black on Copper.

Potassium sulphide, K_2S	6 g.
Ammonia, conc.	5 c.c.
Water	1000 c.c.

Use cold, or only slightly warm.

36. Deep Black on Copper.

Copper nitrate	100 g.
Water	300 c.c.

Immerse the articles or paint on the solution, heat on a hot plate or over a flame to convert the nitrate to oxide. If desired, this treatment may be followed by immersion in

Potassium sulphide	100 g.
Water	1000 c.c.
Hydrochloric acid	10 c.c.

37. Black on Iron or Nickel.

Lead nitrate	90 g.
Ammonium nitrate	60 g.
Water	1000 c.c.

Heat the bath to 60° C., suspend the cleaned articles as anode by iron wire, with lead cathodes, and electrolyze until black. Remove, rinse in hot water, dry in sawdust, and buff or scratch-brush according to the finish desired.

38. Black on Silver or "Oxidized Silver."

Ammonium carbonate	12 g.
Potassium sulphide	6 g.
Water	1000 c.c.

Heat to 80° C. and immerse the articles five to thirty seconds. The deposit will stand scratch-brushing. A one percent solution of barium sulphide acts more slowly.

39. Metallochromes.—Brilliant multi-colored deposits of lead peroxide may be produced upon polished nickel or steel used as anode in solutions of several lead salts.

Caustic soda, NaOH	50 g.
Lead nitrate or acetate	5 g.
Water	1000 c.c.

Dissolve the two solids separately in small amounts

of water, pour the lead solution into the other, then dilute to the proper volume.

For ready reference, data in regard to the foregoing baths have been collected in the table which follows.

TABLE 1

No. of bath	Metal	Bath	Metal per liter		Percent efficiency	E. M. F.	Current density in amperes per	
			Grams	Gram equivalents			sq. dm.	sq. foot
1	Brass	Cyanide	12.8	0.16	65-70	2.7	0.3	2.8
2	Copper	Sulphate	48.4	1.58	98	...	3.2	30.0
3	Copper	Cyanide	6.3	0.10	81	2.9	0.3	2.8
4	Gold	Cyanide	2.0	0.03	95	2.9	0.1	0.9
6	Iron	Sulphate-chloride	51.3	1.83	98	1.0	1.1	10.0
7	Lead	Silicofluoride	$\left. \begin{array}{l} 80.0 \\ 100.0 \end{array} \right\}$	$\left\{ \begin{array}{l} 0.77 \\ 0.97 \end{array} \right.$		...	$\left\{ \begin{array}{l} 1.6 \\ 3.0 \end{array} \right.$	28.0
8	Nickel	Sulphate	11.2	0.38	92	3.5	0.3	2.8
13	Platinum	Pyrophosphate	$\left\{ \begin{array}{l} 2.3 \\ 10.0 \end{array} \right.$	$\left\{ \begin{array}{l} 0.05 \\ 0.20 \end{array} \right.$		3-4	1.0	9.3
15	Silver	Cyanide	2.5	0.23	99	1.3	0.3	2.8
20	Tin	Pyrophosphate	12.2	0.20	99	2	0.2	1.8
21	Tin	Hyposulphite	$\left\{ \begin{array}{l} 15.8 \\ 26.3 \end{array} \right.$	$\left\{ \begin{array}{l} 0.26 \\ 0.44 \end{array} \right.$		...		
24	Zinc	Sulphate-citrate	22.7	0.69	100	2.2	1.0	9.3
26	Zinc	Aluminum sulphate	34.1	1.04	100	...	1.6	15.0

In comparing the metal content of the different baths with the current densities which experience has shown may be safely used, the controlling factor is gram equivalents, not the total weight of metal in the solution.

It is expected that students will consult this table to learn the current densities that should be used for the experiments in plating.

It is the desire of the electroplater to obtain smooth, solid, tough and adherent deposits of metal. This is by no means easy to secure in all cases. Important factors influencing the nature of electrolytic deposits are:

Principles of Electrodeposition

1. The metal deposited.
2. The metal receiving the deposit.
3. The chemical composition of the electrolyte.
4. Gases dissolved in or evolved from the electrolyte.
5. Insoluble impurities.
6. Temperature.
7. Current density.
8. Concentration and circulation of the electrolyte.
9. Thickness of the deposit.
10. Extent of anode surface and arrangement of anodes.

That certain metals have a characteristic form of deposit is illustrated by the spangles in which lead plates out of a solution of its nitrate or acetate, and the needles which silver forms when deposited from a solution of its nitrate.

The difficulty of securing an adherent plating upon highly electro-positive metals, like magnesium or aluminum, is well known. Even zinc is sufficiently electro-positive to cause trouble in plating upon it from many solutions.

The chemical composition of the electrolyte has long been recognized as one of the most important factors. This is attested by the host of formulas extant for the

deposition of a single metal, *e.g.*, nickel. Very minute quantities of material may profoundly affect the nature of the deposit, as recited in the many articles upon the use of addition agents, as such substances are called. Either with or without the use of addition agents it is often important to use a certain salt of the metal in the electrolyte. A change in the electrolyte from an acid to an alkaline reaction, or vice versa, may spoil some metal deposits.

Gas bubbles sometimes cling to the cathode and cause pits as the metal around them grows in thickness. This is especially likely to occur in nickel plating. Another effect of gases is seen in the hardness and brittleness of electro-deposited iron and nickel, which is generally attributed to the absorption of hydrogen by the metal.

A solution free from suspended matter is one of the requisites for good plating from stationary solutions, but in a few cases of deposition on rotating cathodes, such material is added in large amount to produce a polishing effect on the deposited metal. It is the common practice to stir the plating solutions only at the close of the day's work. This removes the layer of dense solution from the bottom of the tank and allows time for the sediment to settle again before the bath is used.

Temperature, current density, concentration and circulation are interdependent factors. The maximum current density allowable without spoiling the deposit seems to depend on the maintenance of enough dissolved metal in actual contact with the cathode to carry whatever current is passing. The rôle of concentration and of stirring is apparent. Rise of temperature increases the rate of diffusion of dissolved substances and so raises the maximum current density permissible in stationary solutions. It has long been customary to use gold and platinum solutions hot. A glance at

Table 1 of page 83 shows that as usually used, these baths stand out from the others as notably deficient in metal. The reason for the better results attained in the deposition of these two metals from hot rather than from cold solutions is obvious. Many platers are now reporting more satisfactory results from a hot than from a cold brass solution. Besides improving circulation, elevation of temperature greatly stimulates corrosion of the anode, and so lessens a recognized difficulty in the operation of the brass bath, viz., poor anode corrosion. Still another effect of high temperatures is to lessen the absorption of hydrogen by nickel and iron, and so permit the production of softer and less brittle deposits of these metals. As the advantages of hot solutions become recognized by platers, they will be used far more generally than at present, in spite of the trouble and cost of heating them.

The stirring of the solutions used in electrolytic analysis has cut down the time required for the deposition of a given weight of metal from about eight hours to fifteen minutes, or even less, but the stirring of plating baths during use has met with little favor on account of the sediment always present in platers' solutions. In the deposition of heavy coatings of silver, the importance of breaking up the film of impoverished solution which forms around the cathode was long ago recognized, and various mechanisms have been used for moving the objects during plating. Similar devices are now coming into use for the rapid production of heavy nickel deposits.

The advantages of a concentrated solution have recently been recognized in nickel plating, and the market is flooded with "high-power" nickel salts, sold under fancy names, which in their essence are only more soluble salts than the sparingly soluble double sulphate of nickel and ammonium which has remained the

standard for so many years. The next logical step would be the use of a hot nickel solution.

It is comparatively easy to obtain fairly smooth deposits of most metals for several minutes, but with continued electrolysis, as the hours, days and weeks (in refining) pass, and the deposit becomes thicker, it loses its original smoothness, and continually grows rougher and more nodular, so that it is an exceptional electrolyte that yields a smooth deposit having a thickness exceeding a half inch. In some plating solutions, the deposit on a polished object becomes dull from incipient roughness in a minute, or less, while in other baths it remains bright for four or five minutes, even though the metal is deposited at the same rate in both cases.

Extent of anode surface is important in maintaining a plating bath in its initial condition as regards acidity, neutrality, etc. As the current density at the anode increases, there is a tendency for the efficiency of corrosion to diminish. When the current efficiency at the anode is less than that at the cathode, there is a production of free acid, free cyanide, etc., in the solution, and when the efficiency at the anode exceeds that at the cathode, the solution tends toward alkalinity. It is evident that by suitable proportioning of the extent of anode and cathode surfaces, it should be possible to maintain the initial condition of the solution.

Since a deposit of uniform thickness is usually desired, the anodes should be arranged so as to distribute the current uniformly over the cathode. With pointed objects and those of irregular shape, this is frequently a matter of considerable difficulty and sometimes requires special anodes, made to conform to the shape to the objects.

An ideal plating bath would possess the following properties:

1. A current efficiency of 100 percent at both anode and cathode.

2. Simple composition, containing only compounds of the metal which is to be deposited.

3. Very soluble metallic salts, so as to permit the use of a high current density, and a corresponding saving in size of the plating equipment.

4. No oxidation or reduction of the dissolved salt as a result of the passage of current. Because of reduction, nitrates are unsuitable as electrolytes either for plating or refining.

5. Low resistance of the solution in order that large currents may be used with an E.M.F. of 6 volts or less.

6. Free solution of the anode under the influence of the current without the formation of a film of oxide or other compound upon it. The anode should, however, not be attacked when the bath is idle.

Since a current efficiency of 100 percent at both electrodes is usually unattainable, the next best condition is to have equal efficiencies at both electrodes, in order that the metal content of the bath may remain unchanged with use. There are a few cases, *e.g.* platinum baths, in which it is not possible to use soluble anodes, and metal must be added from time to time in the form of soluble salts.

While simplicity of composition is desirable, it is often necessary to add foreign substances to overcome defects in the operation of the bath. Acids are added to diminish resistance and to improve the corrosion of the anode. Since the solvent action of the acid is added to the corrosion due to the current, acid solutions frequently show an efficiency at the anode greater than 100 percent. By dissolving the metal already deposited, free acid diminishes the current efficiency at the cathode. With several of the more electro-positive metals having a low

overtoltage for hydrogen, it is probable that the current efficiency in acid solutions is also diminished by the direct deposition of hydrogen instead of metal by the current.

Addition Agents

The use of addition agents has already been referred to page 85. Rapid progress in this important field of study is now being made, and the outlook is encouraging for still greater improvement in the future. Some of the more important papers upon this subject follow:

1. Addition agents in deposition of copper, lead, and silver. Jarvis and Kern, School of Mines Quart., 30:100-129.
2. Addition Agents in Copper Electrolytes containing Arsenic. Wen and Kern, Tr. Am. Electrochem. Soc., 20:120-176.
3. Effect of Addition Substances in Lead Plating Baths. Mathers and Overman, Tr. A. E. S., 21:313-35.
4. Solid Deposits of Lead from Lead Acetate. Mathers, Trans. A. E. S., 24:315-29.
5. Addition Agents in the Deposition of Iron. Watts and Li, Trans. A. E. S., 25.
6. Addition Agents in the Deposition of Zinc from Zinc Sulphate. Watts and Shape, Trans. A. E. S., 25.

Other references are Nos. 2, 12, 13 and 14, page 71 of this book.

The Preparation of Metals for Plating

The preparation of the surface to be plated is a very important and expensive part of plating operations. The brief directions which follow are intended only for laboratory use. For the practice of plating establishments, standard books on plating should be consulted.

General Order of Operations

Remove scale, if present, by grinding or pickling in acid for fifteen to thirty minutes, with occasional

90 A LABORATORY COURSE IN ELECTROCHEMISTRY

scrubbing with a metal-wire brush, rinse, dip in lye, rinse and polish. Hang on sling wire, remove grease in boiling lye or the electric cleaner, rinse thoroughly, and hang in the plating tank immediately. In special cases a momentary dip in weak acid or an amalgamating solution may be required after the removal of grease. Great care must be taken that none of the solutions used in cleaning are carried into the plating baths, or that any of one plating solution gets into another.

Pickle for Removing Scale from Iron or Steel.

Sulphuric acid, conc.	1 part by weight
Water	10 parts by weight

Solution for Iron Rust.

Citric acid	80 g.
Ammonia to make faintly alkaline	
Water to make one liter.	

Requires five to ten hours to remove thick rust with the cold solution, and ten to twenty minutes if the solution is boiling. The iron is not attacked by the fresh solution.

Bright Dip for Brass.

Sulphuric acid, conc.	100 g.	100 c.c.
Nitric acid, conc.	75 g.	100 c.c.
Salt	1 g.	2 g.

Dry brass objects are immersed in this for one second and instantly plunged into cold water. All water must be excluded from the bath.

Lye or Caustic Solution.

Lye 1 lb. per gallon or 120 g. per liter.

To be used boiling hot for the removal of grease from

polished articles. Adhering rouge, etc., may be removed by brushing with a brush made of cotton twine, known as a potash brush. Five to fifteen minutes may be required for the removal of grease. Only animal or vegetable fats are saponified. Mineral oils must be dissolved by benzine, etc. The complete removal of grease is indicated by water flowing from the metal in an even sheet. The student should test the flow of water from the metal before, and several times during treatment with lye. Zinc, aluminum, lead, and all the alloys of the latter are attacked by lye, hence these materials must be immersed only momentarily. The use of the electric cleaner is preferable for such materials.

As a substitute for lye, 1 lb. per gallon of the "Mineral Cleaner" may be used. It is claimed that this removes even mineral oils, and does not injure the hands or clothing.

The Electric Cleaner.

References:

- C. F. Burgess in *Electrical World*, 1898, Vol. 32, page 445.
- C. H. Proctor in *Metal Industry*, Oct., 1905.
- W. L. Churchill in *Metal Industry*, Aug., 1908, page 256.

It has been found that the removal of grease and dirt from metal surfaces by hot alkalies is greatly facilitated by using the object as anode or cathode at very high current densities (40 to 80 amperes per square foot). The action seems to depend mainly on the tearing off of the grease by the storm of gas bubbles liberated on the surface of the metal. When the object is cathode, the alkalinity of the film of solution in contact with the metal must be greatly increased by electrolysis. Some prefer to use the object as anode, others, as cathode; the majority of platers favor the latter practice. With cathode cleaning, it has been found possible to remove

grease in neutral solutions such as sodium sulphate or sodium chloride. This may be advantageous in certain cases, but for metals which are not attacked by lye, it is preferable to use this, or the "Mineral Cleaner" of half the strength that is employed without the current. The author has found the latter material to be very satisfactory, and uses it to the exclusion of lye. Small additions of potassium cyanide were usually made to the earlier electric cleaning solutions used by platers, but this dangerous practice has now become less common.

Polishing.—Rough surfaces may be first ground on an emery wheel, then on leather or felt wheels set up with fine emery powder and glue, and finally polished on cloth wheels or buffs, touched from time to time to a block of tripoli or other polishing composition. For the highest polish after plating, rouge may be used, or lamp black made to a paste with kerosene or alcohol. Deposits of silver, gold and platinum are usually burnished instead of buffed, *i.e.* rubbed down with a polished tool of steel or blood stone, lubricated with soap suds. This saves the usual loss of metal incurred in polishing, and hardens the surface.

In plating on a soft metal like copper with nickel, cobalt or iron, which are very hard when deposited electrolytically, much labor is saved by giving a good polish to the surface to be plated.

For producing a bright, metallic luster, either before or after plating, upon objects with a rough surface, wire wheels or hand brushes should be used. Cloth wheels polish only the high spots.

The remarks which follow upon plating with particular metals call attention to some of the more important points to be observed, but for complete instructions, the books devoted exclusively to plating should be consulted.

Nickel Plating

References:

- Electro-deposition of Nickel—Bennett, Trans. A. E. S., Vol. 25.
- Reactions in Electroplating—Brochet, Metal Industry, Oct., 1908, p. 314.
- Plating with Single Salts—Brass World, June, 1907, page 196.
- Passivity of Nickel Anodes—Schoch, Amer. Chem. Journal, 1909, 43, 235-56.
- Iron in the Nickel Deposit—Bancroft, Trans. A. E. S., Vol. 9, page 217.
- Iron in the Nickel Deposit—Calhane and Gammage, Journal Amer. Chem. S., 1907, 29, 1268-74.
- Deposition of Nickel on Nickel—Snowdon, Trans. A. E. S., 7, 302.
- Deposition of Nickel on Nickel—Blasset, Metal Industry, Sept., 1912, page 375.

For other references on nickeling, see the references on plating in general, page 71.

The electro-deposition of nickel presents several peculiarities. The plating bath must be neutral, or but very slightly acid, else hydrogen is deposited. The reason for this is apparent when the discharge potentials of nickel and hydrogen are compared. From Caspari's value for the overvoltage of hydrogen on nickel, 0.21, the discharge potential of hydrogen on nickel would be -0.12 volts (normal calomel electrode = -0.56 volts). Some values for the discharge potential of nickel by different observers³ are 0.75, 0.80, 0.903 volts. Since the discharge potential of hydrogen on nickel in normal sulphuric acid is much lower than the discharge potential of nickel from normal nickel sulphate, it is evident that if much sulphuric acid be present, the deposit should be mainly hydrogen. The necessity of excluding from

³ Electromotive Force of Nickel—Schoch, Amer. Chem. Journal, 1909, 41, 208-31.

the nickel bath any considerable amount of a strongly dissociated acid is apparent.

The simultaneous deposition of hydrogen with the nickel causes other troubles besides a low-current efficiency. Pitting is troublesome in making heavy deposits of nickel. Here and there bubbles of hydrogen slowly form on the cathode and cling to it, cutting off the current from beneath them, and as the surrounding metal increases in thickness, pits are produced.

Surfaces to be nickeled must be more carefully cleaned than for the deposition of any other metal. The least trace of grease or tarnish on the surface may cause the plate to peel off and roll up into little curls. The brittleness and tendency to curl of electrolytic nickel is generally and probably correctly, ascribed to the alloying of hydrogen with the metal.

The passivity of nickel anodes in certain solutions often causes trouble. Rolled (sheet) anodes are especially liable to become passive in sulphate solutions, resulting in the production of free acid, which in turn affects deposition at the cathode. Since passivity increases with rise of current density, one remedy is to employ a very great anode surface. It has been found that the addition of a little chloride to the bath prevents passivity. The latter remedy according to Langbein, introduces another trouble when nickeling iron. It causes rusting of the iron and separation of the nickel plate. The anodes used should be of the highest purity attainable, and not the cast anodes usually sold by dealers in platers supplies, which contain only ninety or ninety-two percent of nickel, the remainder consisting of iron, carbon, and copper or tin. It has been pointed out that too small an anode surface causes the bath to become acid; too large a surface may, in the presence of the ammonium salts usually used in nickel baths, give it an

alkaline reaction, and cause the production of a dark and poor deposit.

It should be remembered that an absolutely clean surface is indispensable for nickel plating, and once the object has been cleaned, it should be hung in the plating bath as soon as possible and without touching it with the hands. When nickeling brass or copper, the last thing before hanging the object in the plating tank, it is dipped in a solution of potassium cyanide to dissolve any trace of oxide, and thoroughly rinsed. Iron is often coppered before nickeling, but it can be nickeled directly with very satisfactory results provided it is perfectly clean.

Copper Plating

Reference:

The Electro-deposition of Copper—C. W. Bennett,
Trans. A. E. S., Vol. 23, pages 233-50.

Baths used for the deposition of copper are of two kinds, acid and alkaline.

The Acid Copper Bath.—The acid copper bath is used for refining, electrotyping, and wherever a thick deposit or rapid deposition is desired. It cannot be used, however, for plating directly on iron, zinc or tin. The student should consult the table of potentials in sulphate solutions and explain the failure to obtain a satisfactory deposit on these metals. It was found that any considerable amount of free mineral acid could not be used in the nickel bath. The amount of free sulphuric acid used in copper baths varies from two percent in plating solutions, to sixteen percent for some refining solutions. The use of this large amount of acid is possible because copper is below hydrogen in potential, and is but slowly attacked by sulphuric acid. Its purpose is to diminish resistance and improve anode corrosion.

The Alkaline Copper Bath.—Alkaline baths are of two classes, those made up with cyanide, and those containing an alkali tartrate. Since the former are used almost exclusively, the others will not be considered in commenting on the alkaline copper bath.

The basis of the bath is potassium cyanide. The cyanides of most heavy metals are insoluble in water, but unite with potassium cyanide to form double salts which are soluble. The copper bath contains $\text{KCu}(\text{CN})_2$. The particular advantage of the cyanide over the acid electrolyte from the standpoint of the plater, is the ability to plate upon iron, zinc, tin, etc. Another advantage is that the valence of copper is one instead of two, and therefore twice as much copper should be deposited by the same current as in the acid bath. The continuous evolution of hydrogen cuts down the current efficiency, however, and when heavy deposits are desired, after the object has been plated for fifteen to thirty minutes in the alkaline solution, it is removed to the acid bath. Explain the evolution of hydrogen in the alkaline bath, and its failure to appear in the acid solution. The copper cyanide solution plates into hollows and cavities much better than the acid bath, or, to use the technical term, "throws" better.

The chemical action at the anode consists in the union of the cyanogen liberated by the current with the anode, forming cuprous cyanide. Since this is insoluble in water, it forms a coating over the anode which would finally stop the current if not removed. It is therefore necessary to have potassium cyanide in contact with the anode to combine with the cuprous cyanide and convert it into soluble $\text{KCu}(\text{CN})_2$. Cyanide is therefore added in excess of that required to form the double cyanide with all the copper originally in the bath. This is referred to as "free cyanide." Since a solution of

cyanide is slowly converted to potassium carbonate and other compounds by the carbon dioxide of the air, it is necessary to add a little cyanide occasionally.

A trouble to which cyanide baths are subject is "spotting out." Some weeks or even months after plating, small tarnished spots appear, injuring the appearance, and in the case of silvered mirrors, the usefulness also. In the case of plating on cast iron, at least, the trouble seems to be due to electrolyte contained in minute cavities in the metal. The remedy is to destroy the cyanide by repeatedly dipping in dilute acetic acid, alternated with washing in hot water. In other cases, spotting out would seem to be due to the settling of the chemical dust of the plating room upon the work after polishing.

The student should remember that cyanide solutions are extremely poisonous. Objects taken from cyanide baths should not be handled until thoroughly rinsed. The hands should be *thoroughly* washed before leaving the laboratory after working with cyanide plating baths.

The Deposition of Alloys

References:

Conditions which Determine the Composition of Electro-deposited Alloys—S. Field, Trans. Faraday Soc., Sept., 1909, Vol. 5, pages 172–94.

Electrolytic Precipitation of Bronzes—Curry., Trans. A. E. S., Vol. 9, pages. 249–53.

Electrolytic Deposition of Zinc-Nickel Alloys—Schoch, Trans. A.E.S., Vol. 11, pages 135–51.

Watt's Electro-Deposition, pages 534–36.

From experiments with a cyanide brass bath referred to above, Field says, "It is then found that, with a solution containing about equal quantities of the two salts in the absence of any notable amount of free cyanide.

- (1) Copper is more readily deposited, and
- (2) The percentage of zinc increases with the current density.
- (3) The percentage of zinc increases as the amount of zinc compound is increased, while
- (4) Even with a large excess of zinc compound deposits containing a fair proportion of copper are readily obtained.
- (5) The effect of dilution is to raise the percentage of zinc, on account of the higher E.M.F. necessary to maintain the same current density, while
- (6) A rise of temperature induces the deposition of a larger proportion of copper.
- (7) With appreciable amounts of free cyanide the percentage of copper is always high, even with high current density, while the free cyanide adds little conductance to the solution, other than that it prevents the formation of insoluble single cyanides at the anodes."

He summarizes his experiments as follows: "The conclusions drawn from these results are—

1. Brass is deposited quantitatively, or nearly so, over wide ranges of composition from a mixture of cyanides.

2. Even in cyanide solutions the greater ease of deposition of copper is marked in the absence or excess of free cyanide.

3. Conditions tending to raise the E.M.F. increases the percentage of zinc, such as—

- a. Dilution of solution

- b. Decrease of temperature.

4. Anodes are freely soluble with warm, agitated solution even in the presence of only small amounts of free cyanides.

5. The effect of free cyanide is to

- a. Make zinc more positive with respect to copper, and thereby increase the percentage of copper in deposits.
- b. Increase the evolution of hydrogen, and
- c. Induce abnormal anode efficiencies."

The author cannot subscribe to Field's third conclusion. The E.M.F. *per se*, has nothing whatever to do with the composition of the deposit.

From theoretical considerations, the following conditions appear to be of prime importance in the deposition of alloys of two metals:

1. The potentials of the metals in the particular electrolyte chosen should be near together in order that an alloy may be successfully deposited.

2. By regulation of the relative concentrations of the metals, and of the current density, the composition of the alloy may be controlled. Dilution of the solution or increase of current density will cause the deposit to contain a larger proportion of the more electro-positive metal.

3. Stirring causes the deposition of a smaller proportion of the more electro-positive metal (zinc), and has the same effect on the composition as increasing the concentration or lowering the current density.

4. Increase of temperature in stationary electrolytes increases mobility, and therefore should have the same effect as stirring—provided the composition of the electrolyte is not changed at the same time through increased anode corrosion. Pfanhauser, however (page 353), states that the opposite occurs in the brass bath.

5. A moderately dilute electrolyte is a necessity under present current conditions. In the deposition of a single metal, a high content of metal in the electrolyte is desirable since it permits of more rapid deposition than from a dilute solution. A case in point is the modern "hi-power" nickel bath. In depositing alloys the use of very con-

centrated electrolytes will result in an alloy containing too large a proportion of the electro-negative metal. Increase of the current density for the purpose of securing the desired proportion of the electro-positive metal in the alloy will probably result in a "burned" deposit before the proper composition is attained. This should not be taken to mean that no increase in concentration over present practice is possible; but that such increase is more limited than in the deposition of a single metal, and with the stronger solutions, a higher current density must always be used. The farther apart the potentials of the two metals, the more dilute must be the electrolyte.

6. For proper control of the composition of the alloy in practical plating it is desirable that the metals and alloy shall differ in color. The failure of several processes for the electro-deposition of alloys, which otherwise seemed to have good prospects for commercial success, may be laid to their not fulfilling the above condition.

Of the many alloys which have been deposited electrolytically, brass alone is of commercial importance.

Brass Plating

The brass bath has the reputation of being the most difficult of commercial baths to control so that it will yield good deposits of uniform and satisfactory color. The ratio of copper to zinc varies widely in solutions recommended by different platers, but equal weights gives a bath that is probably as easy to control as any.

Anodes should equal or exceed the cathodes in surface, and should be of cast brass. On account of the unsatisfactory corrosion of brass anodes, some platers recommend the use of copper anodes and the addition of zinc salts from time to time. Brass anodes are always left in the bath.

Notes

Too little free cyanide causes a reddish tone to the deposit, and the formation of a thick coating on the anodes.

Too much cyanide causes a vigorous evolution of gas at the cathode, and a slow forming deposit which peels under the scratch brush. Excess of cyanide is particularly to be avoided for plating iron objects.

Langbein advises adding 115 g. per liter of sodium carbonate for maintaining a bright brass color when plating iron or zinc. Old baths are likely to contain much carbonate.

Warm baths (40° – 50° C.) are claimed to give much better results than cold solutions. Rise of temperature should help both circulation and anode corrosion.

Silver Plating

Except for iron, antimony and lead, the metals which it is desirable to plate with silver are electro-positive to this metal in cyanide solutions. The result is that special methods must be used in plating these metals with silver else the bath is decomposed and the object receives by immersion a poorly adherent coating, which later causes the whole deposit to come off.

One of the processes used to secure better adhesion is "quicking." Of this Field (page 228) says:

"Quicking—this term denotes a further preliminary operation of passing the prepared work through a solution of mercury cyanide. Mercury is less positive than either copper or silver. In such a solution, copper, brass and German silver receive a bright deposit of mercury, and when thus covered, the work is *thoroughly rinsed*, and transferred to the silver bath, when, on account of mercury being less positive than silver, no deposition of silver by simple immersion can occur, and the sub-

sequent electrolytic deposit is more adherent." Others ascribe the beneficial effect of "quicking" entirely to an alloying of the mercury with both metals. Thin objects should be immersed in the quick dip only a few seconds as a heavy deposit of mercury may make them brittle. The quicking solution must be entirely rinsed from the objects before transferring them to the silver bath, and if the amalgamated article is a dull gray, it should be rubbed bright with a brush. The quick dip is used on copper, brass and German silver, but is said to be useless for iron, steel or nickel objects.

An alternative process to "quicking" is the use of a special "striking bath" (No. 17, page 77) to form by the current a thin film of silver before plating in the regular bath. The striking bath is very weak in silver and contains a large excess of cyanide. The object is plated in this for only a few seconds.

Langbein says that copper, brass, bronze and German silver may be silvered directly, but that iron, steel, nickel, zinc, tin, lead and Britannia should be coppered or brassed first. Tin and Britannia may be directly silvered by the use of a striking bath.

Silver Direct on Steel vs. Preliminary Nickeling—"All large manufacturers of silver-plated steel cutlery deposit silver directly on steel. Several smaller firms nickel first. Evidence is in favor of the former practice, as many of the large firms used to nickel."⁴

It is recommended that the anodes of purest sheet silver be hung by iron wire. The current should be cut off before removing objects from the bath, else the deposit may have a yellowish tone.

Compare the evolution of hydrogen with that in the other cyanide baths (copper and brass) and explain.

⁴ Brass World, 1912, page 135.

EXPERIMENTS IN PLATING

Deposition by Immersion

EXPERIMENT 66

DEPOSITION OF COPPER ON VARIOUS METALS BY IMMERSION

Prepare 500 c.c. of a nearly saturated solution of copper sulphate. Clean small sheets of aluminum, brass, copper, iron, lead, nickel, tin and zinc. Dip each for a few seconds in the solution, examine and test the adhesion of the deposit, if any. Explain.

EXPERIMENT 67

DEPOSITION BY IMMERSION FROM THE LABORATORY PLATING BATHS

Test the action of the metals of the foregoing experiment on the laboratory plating baths for the deposition of brass, copper (acid and alkaline), lead, nickel and zinc.

EXPERIMENT 68

THE COPPERING OF IRON BY IMMERSION

Prepare a solution containing 50 g. of copper sulphate and 50 g. of concentrated sulphuric acid per liter. This has been recommended⁵ for giving iron a light coating of copper. Test it by immersing clean wire nails. What effect has the time of immersion? How does this deposit compare with that from a saturated solution of copper sulphate in appearance? In adhesion? Explain.

Gore's experiments on deposition by immersion are given in table 7.

⁵ Langbein, 6th edition, page 487.

Plating by Contact.—This method was formerly much used by platers. It consists in placing in the plating solution, in contact with the metal to be plated, pieces of some more electro-positive metal, generally aluminum or zinc. The bath is usually heated.

EXPERIMENT 69

NICKELING BY CONTACT

Heat to 70° or 80° C. a solution containing per liter 30 g. nickel sulphate and 30 g. ammonium chloride. In this immerse the cleaned articles to be plated, in contact with several pieces of aluminum. Stir occasionally. After five minutes, remove the articles and test the durability of the deposit on the polishing wheel. Try using zinc instead of aluminum.

EXPERIMENT 70

TINNING BY CONTACT

This process is used for the tinning of brass pins and other small objects. Boil several small pieces of brass or copper wire in contact with granulated tin in a solution of cream of tartar to which a little stannous chloride has been added. For a thick deposit, zinc should be used in place of the granulated tin. Why? Langbein, page 502, gives as a solution for tinning by zinc contact 10 g. cream of tartar and 27 g. of stannous chloride per liter.

State the advantages of plating by contact. Its disadvantages.

Under the names "Galvanite," "Voltite" and "Nickelite," several plating powders have been put upon the market, which for their operation depend on plating by contact.

Galvanite.—(Electrical Review 1910, Vol. 66 page 243, and Brass World, 1910, page 124, 177, 365.)

This is a paste consisting of the metal (or one of its salts) which is to be deposited, an electro-positive metal such as aluminum, zinc, cadmium or magnesium in a very finely divided state, a substance capable of producing an aqueous electrolyte when brought into contact with moisture, and inert substances such as chalk, soapstone, kieselguhr, boric acid, dextrine, etc., to prevent too rapid action, and to act as polishing powders. The article to be plated is rubbed with a damp cloth containing the paste.

GALVANITE FOR NICKELING

Nickel ammonium sulphate	60 percent
Magnesium	3 percent
Chalk	30 percent
Talc powder	7 percent

FOR GALVANIZING

Ammonium sulphate	15 percent
Zinc dust	45 percent
Magnesium	3 percent
Chalk	30 percent
Talc powder	7 percent

Voltite.—The results of gold and silver plating with this are described in The Metal Industry, 1912, pages 77, 261, and it is claimed that application of voltite for five minutes gave a deposit of silver which it would require four or five hours to deposit in the regular silver plating bath.

EXPERIMENT 71

GALVANITE NICKELING BY ZINC DUST

Prepare galvanite nickeling paste, using zinc dust as the electro-positive metal, and plate pieces of polished

brass and copper. Note the time required for a good looking coating, and plate similar pieces for the same time in the regular nickel bath. Test the deposits with the polishing wheel.

EXPERIMENT 72

GALVANITE NICKELING BY PULVERIZED ALUMINUM

Prepare galvanite nickeling paste with aluminum bronze as the electro-positive metal. Use and test as in experiment 71. Equal parts of nickel sulphate and ammonium chloride will work better than nickel ammonium sulphate. Why?

EXPERIMENT 73

GALVANITE TINNING

Prepare and test a galvanite tin paste after formula No. 20, page 78, with zinc dust. It may be necessary to add some salt to accelerate corrosion of the zinc; what would you suggest?

Plating by Electro-deposition

In experiments on plating, each student should record data such that another could repeat the experiment and obtain the same result. This means securing the facts in regard to the important factors enumerated on page 84.

EXPERIMENT 74

THE EFFECT OF CURRENT DENSITY IN ELECTRO-DEPOSITION

Test the effect of current density in the deposition of nickel from the standard bath, No. 8. Cut a sheet of

copper or brass to fill one end of a rectangular glass jar, polish, and with a knife mark a series of horizontal lines across it, 2 cm. apart. Clean the sheet and immerse it to one of the upper marks. It should fit snugly against the glass, so that the current is confined to one side. Immerse the anode to the same depth at the other end of the jar. For five minutes plate at the current density specified for nickeling. Examine. Raise the cathode to the next mark, raise the anode also, and increase the current fifty percent. Continue in this way until the bottom of the cathode is reached. Compute the current densities, and find that at which the deposit first became dark. Each deposit should be examined before proceeding with the next. Where does the first dark deposit appear? Why there?

EXPERIMENT 75

CIRCULATION AND CRITICAL CURRENT DENSITY

Test the effect of stirring on the solution just used, by putting a mechanical stirrer into the cell and repeating the experiment.

EXPERIMENT 76

CONCENTRATION AND CRITICAL CURRENT DENSITY

Determine similarly the critical current density for the "hi-power" Prometheus nickel solution, without stirring.

EXPERIMENT 77

CRITICAL CURRENT DENSITY IN THE BRASS BATH

After the manner of experiment 74, determine the critical current density for the brass bath. Note the effect of current density on the color of the deposit.

EXPERIMENT 78**THE EFFECT OF CIRCULATION ON THE COLOR OF BRASS
PLATING**

Test the effect of stirring on the color of the brass deposit. Connect two jars of the brass bath in series, put a mechanical stirrer near the cathode in one cell, and plate at 0.3 amperes per sq. dm., or whatever may be the least current that gives a good yellow brass in the stationary solution. Compare the deposits. Repeat at double the former current. At four times the initial current. Explain the results.

EXPERIMENT 79**NICKELING POINTED OBJECTS**

Compare the suitability of nickel bath No. 8, or No. 9 with No. 10 for plating on pointed objects. Cut equal narrow triangles of sheet copper or brass, and plate them on both sides for twenty to thirty minutes with the two baths in series. How can you arrange the anodes to assist in securing an even distribution of the deposit? At the same time plate a similar strip in the large nickel tank in the plating room, without taking any precautions about arrangement of the anodes. The current density should be the same in the large tank as in the others.

EXPERIMENT 80**THE PARTICULAR REQUIREMENT IN A BATH FOR
POINTED OBJECTS**

Why is bath No. 10 especially recommended for pointed objects? Is it due to some specific action of the citrate, or merely because the resistances of the two baths are different? The practical plater controls the bath by

regulation of voltage, and rarely knows what current he is using. Measure the resistivity of each bath, dilute one to the resistivity of the other, and repeat 79, having conditions at the two cathodes as exactly alike as possible. Before closing the switch, consult the laboratory instructor to be sure that you have secured the condition last specified.

EXPERIMENT 81

NICKEL PLATING ON ZINC

Test baths No. 8 or No. 9 and No. 10 for the direct nickeling of zinc. The baths should be in separate circuits instead of in series as in previous cases. Exercise your ingenuity to secure good deposits from both baths. What is the cause of the difficulty in nickeling zinc? In what other ways might it be remedied?

EXPERIMENT 82

THE EFFECT OF TEMPERATURE UPON THE QUALITY OF ELECTRO-DEPOSITED NICKEL

Compare the physical qualities of electrolytic nickel deposited at room temperature, and at 65° to 70° C. Use bath No. 9, or solution from the large plating tank. Operate the two cells in series for forty-five minutes or more at a current density of 0.5 amperes, setting one jar in a tin box, heated by electric lights. Test the deposits for hardness, brittleness and adhesion.

EXPERIMENT 83

UNEVEN DISTRIBUTION OF CURRENT OVER THE CATHODE

Determine the distribution of current over a flat cathode by measuring the thickness of a piece of sheet

110 A LABORATORY COURSE IN ELECTROCHEMISTRY

copper before and after plating in the acid copper bath. Use the large plating solution, and deposit at a current density of 1 ampere for sixty to ninety minutes. Show the distribution of current by a chart. How can a more even distribution of current be secured in plating? Uneven distribution of current is also objectionable in electrolytic refining, where cathodes remain in the electrolyte for many days. Can you suggest precautions for minimizing this trouble?

EXPERIMENT 84

CONCENTRATION CHANGES DURING ELECTROLYSIS

Study the changes in concentration which occur in a plating solution. This may be learned by placing the solution in a glass cell in front of a strong light and examining it during passage of the current. After an hour's operation, considerable changes may have occurred. Is this action helpful or harmful in plating? In refining?

EXPERIMENT 85

PLATING IRON WITH COPPER

Clean a piece of iron and plate it with copper.

PLATING ON ALUMINUM

References:

- Langbein, 6th Ed., page 471
- Wisconsin Engineer, Jan., 1912, pages 162-5.
- A. Fischer, Electrochemical Industry, 1903, page 584.
- Burgess and Hambuechen, Electrochemical Industry, 1904, page 85.
- A. Lodyguine, Trans. A. E. S., 7, 153.
- Loeb's Method, Brass World, 1909, page 145.
- Szarvasy's Method, Brass World, 1909, page 280.
- O. Meyer, Metallurgical and Chem. Eng., 1908, 6, 510.

EXPERIMENT 86

ELECTROPLATING ALUMINUM

Clean a sheet of aluminum 4 by 15 cm. in the electric cleaner, and plate it in the acid copper bath for twenty minutes. Plate another piece of aluminum in the alkaline copper bath. Cut away all the edges and try stripping the deposits. Examine for porosity by transmitted light. Try again, dipping the aluminum in dilute sulphuric acid and rinsing, after treatment in the electric cleaner. Try dilute hydrofluoric acid similarly. In which case is the adhesion best?

EXPERIMENT 87

NICKEL PLATING ON ALUMINUM

Plate aluminum with nickel after the method of experiment 86.

EXPERIMENT 88

PLATING ALUMINUM WITH IRON

Plate aluminum with iron by the above method.

EXPERIMENT 89

PLATING ALUMINUM WITH ZINC

Plate aluminum with zinc by the above method. Compare the adhesion and porosity of the deposits in experiments 86-89. Comment.

EXPERIMENT 90

**THE CURRENT EFFICIENCY OF THE DEPOSITION OF
COPPER**

Prepare a copper coulombmeter⁶ by placing two anodes in a glass cell containing per liter 150 g. copper sulphate,

⁶ Oettel, Exercises in Electrochemistry, pages 16 and 23.

50 g. sulphuric acid, and 50 g. of alcohol. Connect in series the coulombmeter, a cell containing the copper cyanide plating bath, an accurate ammeter and two rheostats. Electrolyze for an hour at a current density of 0.5 amperes, keeping the current constant by adjustment of the rheostats. These should be chosen, one for coarse, the other for fine adjustment of the current. Use two anodes, and a carefully weighed cathode in each cell. At the end of the time, open the switch, quickly remove the cathodes, wash, rinse in distilled water, then in alcohol, dry by hot air, and weigh. From the ampere-hours, compute by Faraday's law the theoretical amount of deposit, and the current efficiency in each cell. Oettel gives 1.182 g. per ampere-hour for the coulombmeter, instead of 1.186 g. required by Faraday's law. How does your result compare with this?

EXPERIMENT 91

THE CURRENT EFFICIENCY OF THE NICKEL BATH

Using the copper coulombmeter and ammeter, find the current efficiency of deposition of the nickel bath used in the laboratory.

EXPERIMENT 92

THE CORROSION OF ALUMINUM ELECTRODES

With the coulombmeter or an ammeter, electrolyze in series for an hour at 0.5 amperes per sq. dm. fifteen percent solutions of sodium chloride, and of potassium sulphate with cleaned and carefully weighed aluminum electrodes, the former at room temperature, and the latter at 50° to 60° C. Use the 110-volt circuit and suitable rheostats for accurate control of the current. The electrodes should be marked for identification before cleaning. Calculate the current efficiency at each electrode. Explain.

EXPERIMENT 93

**THE RELATIVE PROTECTION AFFORDED BY DEPOSITS OF
LEAD AND COPPER**

Plate a cleaned sheet of iron with lead from the silicofluoride solution for a half hour, and plate similarly another sheet with copper. Bend up the edges to form trays, put a little ten percent sulphuric acid in each and observe the protection against corrosion of the iron afforded by the two coatings.

EXPERIMENT 94

THE DEPOSITION OF BRASS

a. Insert a brass anode in a two percent solution of copper sulphate (sp. gr. 1.0126 at 18° C.) and electrolyze long enough to determine the character of the deposit. Add 3 g. of zinc sulphate per 100 c.c. and repeat. Continue additions of zinc sulphate in amounts of 3 g. up to 12 g. per 100 c.c. Record the current and current density used in each case, varying this as you think is best suited to the production of brass. Your conclusions about the deposition of brass from a mixture of the sulphates of zinc and copper?

b. Now dissolve 2 g. copper sulphate and 2 g. zinc sulphate in 100 c.c. of water, stir in 5 g. dry sodium carbonate, and slowly stir in a solution of 10 g. potassium cyanide in 50 c.c. water, until the blue color of the copper salt has disappeared. Test this for the deposition of brass.

Explain the results in (a) and (b).

EXPERIMENT 95

**THE DEPOSITION OF A NICKEL-IRON ALLOY, ABOUT
FIFTY PERCENT**

First consult the table of potentials and report to the instructor on the most promising electrolyte and con-

centration to use. Then test the electrolyte at various current densities. Does the deposit contain both metals? How do the deposits compare with electrolytic iron and nickel in brittleness, curling, hardness, rusting, etc.?

EXPERIMENT 96

DEPOSITION OF A CADMIUM-COPPER ALLOY

Make a preliminary report as in experiment 95. In testing the electrolyte, start with the copper solution of known strength, and to it add the weighed cadmium salt in small amounts, testing the deposit after each addition. How does the process compare with the electro-deposition of the series of zinc-copper alloys?

EXPERIMENT 97

THE DEPOSITION OF A TIN-CADMIUM ALLOY

All tin-cadmium alloys should be white, and the cadmium-rich alloys may possibly make a good protective coating for iron. The alloys in the middle of the series may prove much harder than either metal, and will probably tarnish less readily.

Make a preliminary report on promising electrolytes. If any can be found, try them.

EXPERIMENT 98

"ARCAS" SILVER PLATING—AN ALLOY OF SILVER AND CADMIUM. WATT-PHILIP, PAGE 473

The bath is patented in England (No. 1391 of 1892) by S. O. Cowper-Coles, and is claimed to produce an alloy that is harder, and tarnishes less readily than pure silver. To make the bath, for each liter, dissolve 3.75 g. of silver and 86.7 g. of cadmium in nitric acid, neutralize

by sodium carbonate, precipitate by potassium cyanide, avoiding any excess, wash the precipitate, and then dissolve it in potassium cyanide adding a slight excess of the latter.

Make up 500 c.c. of the bath, and compare the deposit on brass with a silver deposit, as to hardness, smoothness and tarnishing in illuminating gas.

EXPERIMENT 99

DEPOSITION OF A COBALT-NICKEL ALLOY

The alloy containing twenty-five percent cobalt is hardest of the entire cobalt-nickel series of alloys and should be especially valuable for facing electrotypes from which a great number of impressions are desired, or as a substitute for copper in the production of the entire electrotype, provided thick deposits of the alloy can be produced.

Give a preliminary report on a suitable electrolyte. Make up 500 c.c. of the approved electrolyte, deposit on copper in series with a nickel bath, and compare the deposits. Can thick deposits of the alloy be formed without peeling?

EXPERIMENT 100

DEPOSITION OF SILVER FROM NITRATE AND FROM CYANIDE SOLUTIONS

Make up 200 c.c. of a solution of silver nitrate containing the same amount of metal as an equal volume of the laboratory silver-plating bath. Plate on copper with the two baths in series.

EXPERIMENT 101

SILVER PLATING

Plate with silver for fifteen or twenty minutes some small article of your own, or a small sheet of brass.

Compare the appearance of the deposit after one minute with that when finished. Rinse with distilled water, saving the wash water to be added to the plating bath. Burnish or polish the deposit.

EXPERIMENT 102

THE DEPOSITION OF IRON

Set up a cell containing 500 to 600 c.c. of the iron bath, and with anodes of flat bar iron or mild steel, plate on brass or copper for a half hour, examining the deposit occasionally. Test the final deposit for flexibility. Finally put in a cathode of clean sheet iron and run the cell for a week or two. The electrodes should clear the bottom of the jar by an inch to allow for the settling of slime, and the electrolyte should be stirred once or twice daily. Why? If the deposit is thicker upon one part of the cathode than on another, change the position of the electrodes to secure a more uniform distribution of the current. The deposit will be useful as an anode for the production of iron of exceptional purity.

EXPERIMENT 103

DEPOSITION OF CADMIUM FROM A CYANIDE ELECTROLYTE

Dissolve 25 g. of cadmium chloride, $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, in 200 c.c. of water, add 10 g. dry potassium or sodium carbonate, stir in potassium cyanide solution until the precipitate is completely dissolved, and make up to 500 c.c. with distilled water. For the cyanide solution above, dissolve 40 g. in 200 c.c. water, and note the amount required to clear up the precipitate. Keep the remainder to add later if needed to improve the anode corrosion.

Plate for fifteen minutes on polished metal at what you consider a suitable current density. Is the deposit

smooth or rough in comparison with similar deposits of copper, nickel or silver? Determine the critical current density, *i.e.* that at which the deposit becomes rough or dark. Is anode corrosion good or poor? What is the current density at the anode? If necessary, use a larger anode surface or add more cyanide until satisfactory corrosion is secured. Record ratio of anode to cathode area, and total amount of potassium cyanide required for good anode corrosion.

Determine the current efficiency—see experiment 90. What is the valence of cadmium in this solution? On what common metals does cadmium deposit by immersion? Do you think cadmium would be a good or a poor protective coating for iron? Compute the concentration of the bath in grams of metal, and in gram-equivalents per liter.

EXPERIMENT 104

THE "THROWING" OF COPPER

It is always a matter of more or less difficulty to secure a good deposit of metal in the depressions of an article to be plated, and electrolytes differ widely in their ability to deposit metal in such depressions, or in their power of "throwing the metal" as platers say.

Test the "throwing" of copper deposits from the acid and from the alkaline bath.

Fold a piece of paper over the outside of a glass funnel 2 1/2 or 3 inches in diameter, and cut it to fit. With this as a model, cut two sheets of copper, measure their thickness at several points with a micrometer, and fold them to the form of a cone. If small projections are left in cutting, these may be folded over to hold the cone together. Deposition on the outside should be prevented by a coat of paraffine, or a shield of paraffined paper.

The anode should be placed in front of the opening of the cone and 6 inches or more from it. Plate for an hour or more at suitable current densities, and chart the distribution of current over the inside of each funnel.

Metallochromes

Brilliant, multi-colored deposits may be obtained at the anode from solutions of certain lead or manganese salts.

EXPERIMENT 105

METALLOCHROMES FROM SODIUM PLUMBATE

Dissolve 5 g. lead nitrate in 250 c.c. of water, and mix with a solution of 50 g. of sodium hydroxide in an equal amount of water; or formula No. 39 may be used. The colors are most brilliant on a mirror-like surface.

Polish a sheet of copper or brass, flash it for thirty to forty seconds in the nickel bath, and suspend as anode in the above electrolyte. Determine the current density and time required for the most satisfactory results. By using the point of a wire as cathode, at about 1 cm. from the anode, colored rings may be produced. Try stars and circles of wire as cathode.

Oxidizing and Coloring Metals

EXPERIMENT 106

BLACK NICKEL. FORMULA No. 12, PAGE 57

This is widely used for the production of a durable black finish on polished brass and copper. Polish sheets of aluminum, brass, copper, iron and zinc, clean and plate until a good color is obtained. If deposition occurs by immersion, use a high current for a few seconds to "strike" the work. Will the deposit stand gentle

polishing? Bending? The durability of the finish is increased by lacquering.

EXPERIMENT 107

ANTIQUE GREEN ON BRASS. FORMULA No. 30, PAGE 80

This finish is produced without the use of the current.

EXPERIMENT 108

BLACK ON COPPER. FORMULA No. 35

Test the durability of this finish as in experiment 106.

EXPERIMENT 109

BLACK ON COPPER. FORMULA No. 36

Compare this finish with those of experiments 106 and 108.

EXPERIMENT 110

OXIDIZED SILVER. FORMULA No. 38

Silver plate a sheet of polished copper, oxidize it in this solution, and re-polish.

Plate a sheet of polished copper for ten minutes in the acid copper bath to produce a matte surface, plate with silver and oxidize.

EXPERIMENT 111

GALVANOPLASTY

This is the reproduction of objects in metal by electro-deposition. The steps in the process are:

1. The preparation of a cast from the object, usually in wax, gutta-percha or plaster of Paris. The latter must be waterproofed by paraffine or shellac.
2. Rendering the surface a conductor by polishing with

finely pulverized graphite, or by brushing with a solution of silver nitrate, followed by a solution of potassium sulphide, or fuming in hydrogen sulphide to form a film of silver sulphide.

3. Deposition of a thin sheet of copper upon the prepared surface, requiring ten to twenty hours in the acid copper bath. The metal shell is then removed, and may be filled with melted lead or solder, and a light deposit of any desired metal may be given to the whole.

For details of the process, consult Langbein or Pfanhauser.

By this method reproduce a medal or some similar object. When finished, it may be oxidized, and the color buffed off the high portions so that they stand out against the darker background.

EXPERIMENT 112

THE ELECTROPLATING OF WOOD, LEAVES, ETC.

Give the object two coats of very thin shellac, treat with silver nitrate and hydrogen sulphide as above and plate in the copper bath. It may be necessary to repeat the process for the formation of silver sulphide several times before attempting to plate with copper. Only simple objects like oak or holly leaves should be attempted at first.

Electrolytic Preparations

References:

Allmand—Applied Electrochemistry, pages 116–135, 144–147, 386–406.

Elbs—Electrolytic Preparations, pages 6–15, 89–90.

Lehfeldt—Electrochemistry.

Perkin—Practical Methods of Electrochemistry, pages 82, 195–199, 250–251.

Thompson—Applied Electrochemistry, pages 67–79.

Oxidation and Reduction

Allmand, pages 129–132.

Thompson, pages 73–74.

Electrolysis lends itself especially well to oxidation and reduction processes, since it is possible to vary not only the speed, but also the intensity of the action with great nicety. This often permits the reduction of one substance in the presence of a second reducible compound. Factors affecting the intensity of the reducing action are the material of the electrode, the nature of its surface, and the current density. In comparing the effects of different cathodes, an attempt is frequently made to resolve the reducing action of electrodes into the catalytic

TABLE 2.—OVERVOLTAGE OF HYDROGEN

Cathode	By Caspari ⁷ N.H ₂ SO ₄	By Foerster and Piguet ⁸ N.H ₂ SO ₄				Discharge potentials N.H ₂ SO ₄	
		Least potential	Current 0.04 amp./cm. ²	2N.H ₂ SO ₄ 0.125 amp./cm. ²	By Tafel ⁹ 0.1 amp./cm. ²	From Caspari	From Foerster
Mercury	0.78	0.43	1.25	1.32	1.30	+ .5476	+ .1976
Zinc	0.70					+ .4676	
Lead	0.64	0.35	1.26	1.35	1.30	+ .4076	+ .1176
Tin	0.53	0.43	1.08	1.16	1.15	+ .2976	+ .1676
Cadmium	0.48	0.48	1.18	1.23	1.22	+ .2476	+ .1976
Palladium	0.46					+ .2276	
Copper	0.23	0.10	0.67	0.79	0.79	– .0024	– .1324
Nickel	0.21	0.10	0.64	0.74	0.74	– .0224	– .1324
Silver	0.15				0.93?	– .0824	
Platinum	0.09	0.07				– .1424	– .1624
Gold	0.02	0.055	0.86	0.96	0.95	– .2124	– .1874
Platinized-platinum.	0.0	0.005	0.05	0.07	0.07	– .2324	– .2274

⁷ Z. phys. Chem., 1899, 30, 89.

⁸ Z. f. Elektrochem., 1904, 10, 715.

⁹ Z. phys. Chem. 1904, 50, 712.

122 A LABORATORY COURSE IN ELECTROCHEMISTRY

action of the electrode material, and what is called the overvoltage of hydrogen. Current density is supposed to affect only the latter.

The variation in the potential required by electrodes of different metals for visible evolution of hydrogen is usually expressed as the "overvoltage of hydrogen" on that particular metal, the least potential of platinized platinum for hydrogen evolution being taken as zero. Table 2 gives values of the overvoltage of hydrogen obtained by different observers. The effect of current

TABLE 3.—ANODE POTENTIALS AND OVERVOLTAGE OF OXYGEN

Anode	By Coehn ¹⁰ Least anode potential for evolution of O ₂ vs. hyd. electrode in N-KOH,	Overvoltage Allmand, page 131	Discharge poten- tial vs. calomel electrode calc. by author	By Foerster, ⁸ Least potential for evolution hyd. vs. hyd. electrode. 2N KOH	D _A = 0.033 amp./cm ² .		
					2N KOH after 2 hours, 15° C.	2N KOH, 99° C.	2N H ₂ SO ₄ , 99° C.
Nickel, sponge.	1.28	0.05	-0.9524				
Nickel, smooth.	1.35	0.12	-1.0224	1.35	2.00	1.77	
Cobalt....	1.36	0.13	-1.0324				
Iron.....	1.47	0.24	-1.1424	1.47	2.02	1.89	
Platinized Pt.	1.47	0.24	-1.1424	1.47	2.30		
Copper....	1.48	0.25	-1.1524				
Lead.....	1.53	0.30	-1.2024				
Silver.....	1.63	0.40	-1.3024				
Cadmium..	1.65	0.42	-1.3224				
Palladium..	1.65	0.42	-1.3224	1.65	2.45		
Platinum..	1.67	0.44	-1.3424	1.67	2.92	2.50	2.17
Gold.....	1.75	0.52	-1.4224				

density is also shown. The discharge potentials, referred to the calomel electrode (value -0.56 volt)

¹⁰ Coehn and Osaka—Z. Anorg. Chem., 1903, 34, 86.

have been calculated by the author from the values for overvoltage by the use of Wilsmore's value 0.3276 volts for the difference between the calomel electrode and the hydrogen electrode in normal sulphuric acid.¹¹

Oxygen shows similar overvoltage effects upon anodes of different materials, as shown in table 3.

The increase of overvoltage with time and its diminution with rise of temperature varies for different metals.

EXPERIMENT 113

THE EFFECT OF CATHODES OF DIFFERENT METALS ON THE REDUCTION OF POTASSIUM NITRATE

Text the reducing action on normal potassium nitrate solution of cathodes of platinized platinum, smooth platinum, and polished zinc. These experiments may most conveniently be carried out by connecting a standard oxyhydrogen coulombmeter in series with the same apparatus (see experiment 25) containing the special cathode. If a coulombmeter is not available, a cell may be made from two wide mouth bottles fitted with two-hole rubber stoppers. One hole of each carries a short glass tube connecting the bottles, and through the other hole passes a glass tube connected to a gas burette or other device for collecting gases. The electrodes are carried by stout wires passing through the stoppers.

By means of the gas coulombmeter, or an accurate ammeter placed in series with the experimental cell, determine the hydrogen equivalent of the current used. From this and the volume of gas collected, determine what percent of the current was spent in reduction with each cathode.

¹¹Lehfeldt, page 240.

EXPERIMENT 114**THE OXIDATION OF LITHARGE TO LEAD PEROXIDE.
PERKIN, PAGE 215**

The electrolyte, consisting of a twenty percent solution of sodium chloride, should be placed in a rectangular battery jar, with an anode of platinum or graphite and a cathode of lead or graphite. The current density at the anode may be 1 to 1.5 amperes. The cathode should be wrapped in parchment or cloth (why?) and the electrolyte must be stirred vigorously during electrolysis to keep the litharge in suspension. Use 25 g. of finely pulverized litharge. This becomes darker in color as electrolysis proceeds, and when it is all converted to the peroxide, the color is a dark brown.

After passing the current for the number of hours required by theory, collect the product on a filter, wash it free from chloride, and warm it with dilute nitric acid to remove any unaltered litharge, wash, dry and weigh. Ascertain the total yield, grams per ampere-hour and the current efficiency. No chlorine is liberated during electrolysis, since sodium hypochlorite is formed, and it is this mainly which oxidizes the litharge.

EXPERIMENT 115**LEAD PEROXIDE FROM LEAD NITRATE**

Dissolve 38 g. lead nitrate in 500 c.c. of water, and 12 g. of caustic soda in 400 c.c. of water. Mix the solutions, add 100 g. of salt and 2 g. of potassium chromate, start the stirrer, electrolyze and purify as before. The purpose of the chromate is to form a diaphragm of chromium hydrate over the cathode, and so lessen reduction of the hypochlorite by nascent hydrogen. The cathode need not be covered with parchment in this ex-

periment. Compare the yield and current efficiency with the results in the previous experiment. To what do you ascribe the difference? To insure the same current in both experiments, they may be run in series.

EXPERIMENT 116

LEAD PEROXIDE FROM LEAD BY LUCKOW'S PROCESS.
ALLMAND, PAGE 389

Use weighed electrodes of sheet lead and an electrolyte containing 15 g. per liter of a mixture of 99.5 parts sodium sulphate and 0.5 parts sodium chlorate, slightly acidified with sulphuric acid. Determine the current efficiency and the actual yield. What are the defects of the process? The effect of different current densities may be investigated.

EXPERIMENT 117

POTASSIUM PERSULPHATE. ELBS, PAGE 138;
PERKIN, PAGE 202

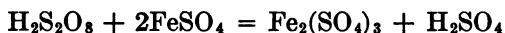
This preparation requires that the temperature be kept below 20° C. and a better yield is obtained below 10° C. The electrolyte consists of a saturated solution of potassium bisulphate, the strength of which is maintained by suspending crystals of KHSO_4 in a perforated vessel in the upper part of the electrolyte. The anode consists of a spiral of platinum wire of 1 to 2 sq. cm. surface, sealed into a glass tube and placed near the bottom of the electrolyte. This should be surrounded by a wide glass tube open at both ends, and the cathode of platinum or lead should surround this tube near the surface of the electrolyte, which is contained in a very tall, narrow beaker, placed in a large dish of ice water. The current density at the anode should be between 500 and 1000

amperes per sq. dm. and that at the cathode as low as possible to minimize heating. Mueller finds that the yield of persulphate is increased by adding small amounts of hydrofluoric acid; this requires the use of hard rubber or paraffined glass apparatus.

As soon as the electrolyte becomes saturated with the slightly soluble persulphate, the solid salt begins to separate. After a considerable amount has formed, collect and dry the product with the aid of a filter pump, and complete the drying over sulphuric acid *in vacuo*. Determine its purity, and the current efficiency.

The Estimation of Persulphuric Acid

To the solution of persulphuric acid, add a known amount of a solution of ammonio-ferrous sulphate, and titrate the excess of this by permanganate.



For persulphates, the addition of ferrous sulphate should be followed by one-half volume of dilute sulphuric acid and 100 c.c. of boiling water, and the solution should be titrated by permanganate at once. Potassium or sodium persulphate may be estimated by determining the loss of weight on ignition.



The preparation of ammonium persulphate requires a diaphragm, but is more satisfactory than the previous experiment. A diaphragm may be used in the preparation of potassium persulphate with good results.

EXPERIMENT 118

AMMONIUM PERSULPHATE. ELBS, PAGE 35;
PERKIN, PAGE 204

The electrodes, current density and temperature are as in the previous experiment, except that the cathode

may be a lead tube carrying cold water. A porous cup, boiled for several hours in water to expel the air, serves as a diaphragm and contains the anolyte—the solution surrounding the anode—which consists of 2 percent sulphuric acid saturated at 10° C. with ammonium sulphate. The strength of the anolyte is maintained as in experiment 117. To diminish its resistance, the porous cup should be allowed to soak in the anolyte over night. The catholyte consists of 1 volume of concentrated sulphuric acid to 1 1/2 volumes of water. The anolyte may be regenerated after use by the addition of ammonia saturated with ammonium sulphate, the catholyte by the addition of sulphuric acid. Proceed with the electrolysis, collection of the product and titration as in experiment 117.

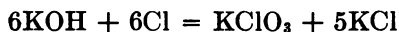
EXPERIMENT 119

POTASSIUM CHLORATE FROM POTASSIUM CHLORIDE.

ELBS, PAGE 26, 29–31; PERKIN, PAGE 210;

HOSTELET, PAGE 79

The electrolyte consists of 100 g. potassium chloride, 1 g. potassium carbonate, and 1 g. potassium dichromate dissolved in 250 c.c. of warm water. The anode should be platinum gauze or sheet, and the cathode a sheet of platinum, nickel, copper or graphite. The electrodes should be placed 1 cm. apart. The current density at the anode should be 20 amperes per sq. dm., but at the cathode should be greater. Why? During electrolysis the electrolyte should be maintained at a temperature of 50° to 60° C. kept faintly acid by a stream of carbon dioxide, and gently stirred. Air may be used for stirring.



One ampere-hour liberates 1.322 g. of chlorine. Compute

the amount of potassium chlorate which should be formed per ampere-hour. Pass 100 to 400 ampere-hours, using a coulombmeter or recording ampere-hour meter in series with the cell. Potassium chloride should be supplied from a bag or perforated cup hung in the upper part of the cell.

After cooling, collect the potassium chlorate, recrystallize it once, and weigh it. Evaporate the mother liquor from the cell to half its volume and cool it. Recrystallize this product also. Instead of evaporating the contents of the cell, the amount of dissolved chlorate may be determined by volumetric analysis. For the solubilities of potassium chloride and potassium chlorate, see Elbs, page 27. State the current efficiency based on the total amount of chlorate formed. It should exceed 70 percent until over half the chloride has been converted to chlorate.

EXPERIMENT 120

PREPARATION OF OTHER CHLORATES

The chlorates of sodium, barium, calcium and strontium may be prepared in a manner similar to that for potassium chlorate, but since these chlorates are very soluble, it is difficult to separate them from the chlorides. Prepare barium or sodium chlorate. How does the current efficiency compare with that of potassium chlorate? How could you make the latter from your electrolyte? How can you prepare a solution of copper chlorate from your product?

EXPERIMENT 121

POTASSIUM BROMATE FROM POTASSIUM BROMIDE. ELBS, PAGE 28; PERKIN, PAGE 212

The electrolyte consists of 125 g. potassium bromide, and 1 g. potassium chromate in 500 c.c. of water. What

is the purpose of adding the chromate? The anode should be platinum gauze or sheet and the cathode a sheet of platinum or nickel. The current density at the electrodes should be between 10 and 12 amperes per sq. dm. and the temperature 40° C.



One ampere-hour liberates 2.982 g. of bromine. Calculate the amount of bromate that should be produced per ampere-hour. Pass 125 to 150 ampere-hours, evaporate to 0.4 volume, and cool. Collect and dry the bromate by aid of the filter pump. The current efficiency should be ninety percent, and the material yield about seventy percent of the theoretical amount.

100 parts of water dissolves

3.1 parts potassium bromate at 0° C.

7.0 parts potassium bromate at 20°

22.8 parts potassium bromate at 60°

49.8 parts potassium bromate at 100°

EXPERIMENT 122

POTASSIUM IODATE FROM POTASSIUM IODIDE

Use as electrolyte 25 g. potassium iodide, 1 g. potassium hydrate and 0.2 g. potassium chromate per 100 c.c. at 25° to 30° C., with other conditions as for potassium bromate.

100 parts of water dissolves

4.7 parts potassium iodate at 0° C.

8.1 parts potassium iodate at 20°

18.5 parts potassium iodate at 60°

32.2 parts potassium iodate at 100°

Sodium iodate is prepared similarly and is only slightly more soluble. Which, then, can probably be prepared at the higher current efficiency? Why?

EXPERIMENT 123

POTASSIUM PERCHLORATE. ELBS, PAGE 33; PERKIN, PAGE 214.

The electrolyte consists of a saturated solution of potassium chlorate, with a perforated vessel or bag containing crystals of the same salt suspended near the top of the cell. The anode consists of platinum gauze or sheet, and the cathode of a sheet of platinum or copper. The current density at the anode should be less than at the cathode, and may be from 8 to 12 amperes per sq. dm. The temperature must be kept below 25° C., and the efficiency is better if a temperature of 10° C. is maintained. Occasional but not continuous stirring is advantageous. A current efficiency of about eighty percent may be attained.

100 parts of water dissolves

0.7 parts potassium perchlorate at 0° C.

6.4 parts potassium perchlorate at 50°

19.9 parts potassium perchlorate at 100°

Potassium perchlorate may be prepared with a current efficiency of ninety percent by electrolysis of a solution containing per liter 300 to 500 g. of sodium chlorate, and at the end of the experiment adding a quantity of a cold saturated solution of potassium chloride corresponding to the ampere-hours passed.



Each 100 g. of perchlorate requires 61 g. potassium chloride, or 190 c.c. of a solution of the chloride saturated at 20° C. Should the electrolyte become alkaline during electrolysis, it should be made faintly acid by the addition of a few drops of dilute sulphuric acid.

EXPERIMENT 124**BARIUM PERCHLORATE. ELBS, PAGE 34**

Electrolyze as in experiment 123 a cold solution containing 300 g. barium chlorate, $\text{BaClO}_3 \cdot \text{H}_2\text{O}$ per liter. The current efficiency exceeds seventy percent at the outset, but drops to twenty percent after ninety percent of the chlorate has been changed to perchlorate. What should be the effect of stirring at the anode at this stage of the electrolysis? Since both salts are very soluble, a separation of the two in aqueous solution is not practicable. Evaporate to dryness on a water bath, and extract the residue with hot ninety-five percent alcohol, in which the perchlorate is readily soluble, but the chlorate and chloride are almost insoluble. Cautiously distil off the alcohol. Mixtures of combustible substances with chlorates or perchlorates may be exploded by heat or percussion. Strong and sudden heating of perchlorates should be avoided as several of them are explosive.

Barium perchlorate is especially useful for the preparation of perchlorates of other metals for use in electroplating, for which purpose the perchlorates are proving particularly advantageous. Outline a method for preparing a solution of copper perchlorate from barium perchlorate.

EXPERIMENT 125**OXIDATION OF CHROMIUM SULPHATE TO CHROMIC ACID. ELBS, PAGE 17**

Use as anode a sheet of lead previously per-oxidized by use as anode in dilute sulphuric acid. The cathode of sheet lead should be placed in a porous cup which is surrounded by the anode. The anolyte consists of 150 c.c. of concentrated sulphuric acid, 200 g. of chrome

alum, $\text{KCr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, per liter. This is prepared by pouring the acid slowly into about 750 c.c. of water, and stirring in the powdered alum. The catholyte may consist of one volume of sulphuric acid to four volumes of water. The temperature should be from 50° to 60°C . and the current density at the anode 2 to 3 amperes per sq. dm. How could you raise the current density at the anode without lessening the current efficiency? What should be the current density at the cathode?



Stir every half hour and draw out a sample for titration, which can be performed by adding excess of carefully weighed ferrous ammonium sulphate, and titrating with permanganate. The theoretical yield is 1.25 g. CrO_3 per ampere-hour. Maintain the current constant, and plot curves of current efficiency and of grams CrO_3 per liter vs. time. The current efficiency should exceed ninety percent until most of the chromium salt has been oxidized.

EXPERIMENT 126

CUPROUS AND CUPRIC HYDROXIDES OR OXIDES FROM COPPER. ELBS, PAGE 40; PERKIN, PAGE 220

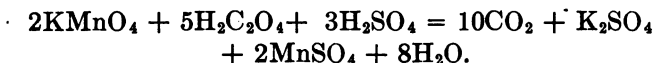
Arrange two cells in series, one containing a thirteen percent solution of sodium chloride, the other a sixteen percent solution of crystallized sodium sulphate. The copper anodes and iron cathodes should be 4 cm. apart, and the same distance from the bottom of the cells. The anodes should be enclosed in cloth bags or wrapped in parchment. Why? The electrolyte should be stirred. At room temperature the hydroxides are formed, but at 100°C ., the products are the oxides. Wash, dry and weigh the oxides, determine the anode corrosion, the current efficiency at the anode, and the current

efficiency of the process. What would be the cost of electric energy at 10 cents per kilowatt hour for a pound of each product according to the conditions of this experiment? What data do you need besides the ampere-hours per pound of product in order to answer the last question? See that the necessary data are obtained during the experiment.

EXPERIMENT 127

POTASSIUM PERMANGANATE. PERKIN, PAGE 218

Manganese or ferro-manganese serves as anode in a forty percent solution of potassium carbonate, specific gravity 1.42. The cathode of sheet iron must be placed in a porous cup. Iron is precipitated as hydroxide. The current efficiency may be followed by titrating with oxalic acid.



Find the anode corrosion and the amount of permanganate produced. Plot the curve of grams of permanganate against ampere-hours or time. If a plate of copper oxide or the positive plate of a storage cell be substituted for the iron cathode, the porous cup may be omitted. Why is this? The yield is poor.

EXPERIMENT 128

POTASSIUM CHROMATE. PERKIN, PAGE 219

By the method of the previous experiment, potassium chromate may be made by using an anode of ferro-chromium and potassium hydrate as electrolyte. The progress of electrolysis may be followed by occasional titration of a sample with permanganate after the addition of an excess of ferrous ammonium sulphate and sulphuric acid.

134 A LABORATORY COURSE IN ELECTROCHEMISTRY



The yield is good. Find the current efficiency at the anode as well as of the production of chromate.

EXPERIMENT 129

THE REFINING OF MERCURY. HOSTELET, PAGE 88

As electrolyte prepare a solution of mercurous nitrate by the action of nitric acid on excess of mercury. Place the mercury to be purified as anode in a small crystallizing dish set in a larger one. As cathode use a platinum wire or purified mercury in the outer dish. The current density at the anode may be 1 to 1.5 amperes per sq. dm. To prevent the solution about the anode from becoming saturated, it should be stirred occasionally. Determine the current efficiency at anode and cathode. Assuming that the impure mercury from use in the laboratory had dissolved traces of cadmium, copper, gold, silver, and zinc, which of these impurities would still be found in the anode, and which in the electrolyte at the end of the experiment? Why?

EXPERIMENT 130

SCHEELE'S GREEN, CuHAsO_3 . POISON!

As electrolyte use 10 g. of crystallized sodium sulphate per liter, with electrodes of sheet copper placed far apart, and suspend near the cathode a cloth bag containing arsenious oxide. Use a current density at the anode of 2.5 amperes per sq. dm., and stir vigorously. The products of electrolysis are copper sulphate and caustic soda. The latter dissolves arsenious oxide, forming sodium arsenite, Na_3AsO_3 , which reacts with the copper sulphate to form Scheele's green. Determine the loss

of weight of anode, the efficiency of anode corrosion, and the amount of Scheele's green produced per ampere-hour. Discuss the convenience and cost of the electrolytic vs. the chemical manufacture of this compound.

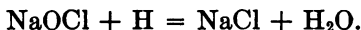
EXPERIMENT 131

SODIUM HYPOCHLORITE FROM SALT. ELBS, PAGE 21;
PERKIN, PAGE 207

When a strong solution of sodium chloride is electrolyzed cold without a diaphragm, the main product is sodium hypochlorite.



As soon as hypochlorite is present in considerable amount it reaches the cathode and is reduced.



Since this reduction is caused only by nascent hydrogen, a high current density at the cathode is desirable.

With low current density at the anode, there is practically no evolution of gas at first, but as the proportion of hypochlorite increases, oxygen is evolved at the anode, since hypochlorite is more readily decomposed than chloride. With high current density at the anode, the solution about the anode is kept impoverished in ClO ions, and this undesirable reaction is at a minimum.

As electrolyte use 500 to 1000 c.c. of a clear, saturated solution of salt, an anode of platinum, nickel or graphite. The current density at the anode should be 12 to 16 amperes, and that at the cathode 20 to 30 amperes per sq. dm. The temperature should be between 15° and 20° C. Above 25° C. there is formation of chlorate.

Circulation may be induced by placing the anode on one side of the cell near the top and the cathode on the other side near the bottom. Maintain a constant known

current, and every half hour stir, remove 10 c.c. of the electrolyte and titrate by adding excess of potassium iodide, acidifying strongly with acetic acid, and estimating the free iodine by tenth normal sodium thiosulphate. Hydrochloric acid must not be used for acidifying, as is often recommended, since this slowly decomposes any chlorate present.

Plot curves of current efficiency against time, and against the percent of hypochlorite formed. For the method of determining the percent of the total current which is wasted by reduction and in the useless evolution of oxygen at the anode, consult either of the references cited above.

The addition of 0.5 percent of sodium or potassium chromate causes the formation of a film of chromium hydrate over the cathode, which greatly lessens the undesirable reduction of hypochlorite. A second experiment may be tried with this addition.

EXPERIMENT 132

THE OXIDATION OF POTASSIUM FERROCYANIDE TO THE FERRICYANIDE. V. HAYEK¹²

A diaphragm is required and the anode compartment should have twice the volume of the cathode compartment. The anolyte should be well stirred continuously, and should be kept faintly alkaline and at a temperature of 25° C. Electrodes of nickel gauze or sheet may be used, with an anode current density of 0.3 to 1.5 amperes per sq. dm., depending on circulation and the concentration of the solution, which may be from ten percent to saturation.

After complete conversion to the ferricyanide, as shown by its no longer producing a blue precipitate with a

¹² Z. anorg. Chem., 1904, 39, 240.

drop of a solution of a ferric salt, crystallize and weigh the product. Find the material yield and the current efficiency.

EXPERIMENT 133

**POTASSIUM FROM POTASSIUM HYDRATE. HOSTELET,
PAGE 70**

Melt down to quiet fusion in an iron crucible 400 to 500 g. of potassium hydrate. In about two hours it should be ready to electrolyze. Thrust the cathode of iron wire 3 mm. in diameter through a hole in the bottom of a magnesia crucible and invert this in the electrolyte. As anode use a sheet of iron. Explosions occur at first, due to the burning of the potassium in the air contained in the crucible. Fifteen amperes have given 12 to 13 g. of potassium per hour, a yield of about fifty-eight percent. On stopping electrolysis, allow the cell to cool, and remove the crucible containing the potassium only just before it would freeze into the electrolyte, and plunge it into kerosene to cool.

APPENDIX

TABLE 4.—ATOMIC WEIGHTS AND ELECTROCHEMICAL
EQUIVALENTS

	Atomic weight	Valence	Grams per amp.- hour		Atomic weight		Grams per amp.- hour
Aluminum	27.1	3	0.3368	Magnesium	24.3	2	0.4531
Antimony	120.2	3	1.4966	Manganese	54.9	2	1.0255
Arsenic	74.9	3	0.9324	Mercury	200.6	1	7.4803
Barium	137.4	2	2.5619	Molybdenum	96.0	2	1.7900
Bismuth	208.0	3	2.5854	Nickel	58.7	2	1.0945
Bromine	79.9	1	2.9814	Nitrogen	14.0	3	0.1745
Cadmium	112.4	2	2.0955	Oxygen	16.0	2	0.2983
Calcium	40.1	2	0.7477	Palladium	107.0	2	1.9951
Carbon	12.0	4	0.1118	Platinum	195.2	4	1.8206
Chlorine	35.5	1	1.3220	Potassium	39.1	1	1.4584
Chromium	52.0	3	0.6476	Silicon	28.3	4	0.2638
Cobalt	59.0	2	1.1000	Silver	107.9	1	4.0248
Copper	63.6	2	1.1858	Sodium	23.0	1	0.8596
Fluorine	19.0	1	0.7085	Strontium	87.6	2	1.6333
Gold	197.2	3	2.4513	Sulphur	32.1	2	0.5980
Hydrogen	1.008	1	0.03759	Tin	119.0	2	2.2188
Iodine	126.9	1	4.7303	Titanium	48.1	4	0.4490
Iron	55.8	2	1.0404	Tungsten	184.0	2	3.4308
Lead	207.1	2	3.8613	Zinc	65.4	2	1.2194
Lithium	6.9	1	0.2622				

26. 817 ampere-hours deposit one gram-equivalent of any substance.

TABLE 5.—RESISTIVITY OF METALS. MICROHMS PER CM².

At 0° C.		Resis- tivity	Temp. coeff. for 1° C.			Resis- tivity	Temp. coeff. for 1° C.
Aluminum	Annealed	2.8	0.0046	Nickel	Annealed	12.4	0.00538
Antimony		36.0		Nichrome		95.5	0.00043
Arsenic		33.3		Platinum	Annealed	9.0	0.00341
Bismuth		130.0	0.0035	Silver,		1.50	0.00377
Copper	Annealed	1.58	0.0039	Tin		10.0	0.00428
Gold	Annealed	2.0	0.0037	Zinc		5.6	0.00365
German silver.		20.8	0.0004				
Iron	Annealed	9.5	0.0058				
Lead		19.0	0.0038				
Mercury		94.2	0.00072				

TABLE 6.—RESISTIVITY OF ELECTROLYTES. KOHLRAUSCH & HOLBORN

H ₂ SO ₄ at 18° C.	Grams acid in 100 g. of sol.	Specific gravity	Resistivity	Temp. coefficient for 1° C.	Gram equivalents per liter
	1		21.93	0.00112	0.204
	2.5	1.0161	9.24	0.00115	0.519
	5	1.0331	4.82	0.00121	1.065
	10	1.0673	2.57	0.00128	2.182
	15	1.1036	1.85	0.00136	3.384
	20	1.1414	1.54	0.00145	4.667
	30	1.2207	1.36	0.00162	7.487
	40	1.3056	1.48	0.00178	10.68
	50	1.3984	1.86	0.00193	14.30
	60	1.5019	2.70	0.00213	18.42
	70	1.6146	4.67	0.00256	23.11
	80	1.7320	9.13	0.00349	28.33
	85	1.7827	10.30	0.00365	30.98
	90	1.8167	9.38	0.00320	33.43
	95	1.8368	9.84	0.00279	35.68
	97	1.8390	12.50	0.00286	36.47
	99.4	1.8354	118.00	0.00400	37.22

TABLE 6.—RESISTIVITY OF ELECTROLYTES.—*Continued.* KOHL-
RAUSCH & HOLBORN

HCl at 10°	G. HCl per 100 g. of sol.	Specific gravity	Resistivity	Temp. coefficient for 1° C.	Gram equivalents per liter
	5	1.0242	2.55	0.00159	1.408
	10	1.0490	1.59	0.00157	2.884
	15	1.0744	1.35	0.00156	4.431
	20	1.1001	1.32	0.00155	6.050
	25	1.1262	1.39	0.00154	7.741
	30	1.1524	1.52	0.00153	9.506
	35	1.1775	1.70	0.00152	11.33
	40	1.2007	1.95		13.22
KOH at 15°	4.2	1.0382	6.85	0.00188	0.619
	8.4	1.0777	3.69	0.00187	1.580
	12.6	1.1177	2.67	0.00189	2.515
	16.8	1.1588	2.20	0.00194	3.477
	21.0	1.2088	1.97	0.00200	4.534
	25.2	1.2439	1.86	0.00210	5.599
	29.4	1.2908	1.85	0.00222	6.778
	33.6	1.3332	1.92	0.00237	8.001
	37.8	1.3803	2.10	0.00258	9.319
	42.0	1.4298	2.39	0.00284	10.730
KCl at 18°	2.4	1.0135	29.10	0.00219	0.33
	5.0	1.0308	14.63	0.00202	0.693
	8.0	1.0519	8.20	0.00200	1.13
	10.0	1.0638	7.42	0.00189	1.43
	15.0	1.0978	4.99	0.00180	2.26
	19.3	1.1308	3.83	0.00171	2.93
	20.0	1.1335	3.77	0.00169	3.05
	25.0	1.1408	3.59	0.00167	3.83
KI at 18°	5.0	1.0363	29.76	0.00206	0.312
	10.0	1.0762	14.81	0.00201	0.650
	20.0	1.1679	6.94	0.00158	1.410
	30.0	1.2730	4.38	0.00167	2.307
	40.0	1.3966	3.18	0.00152	3.374
	50.0	1.5450	2.57	0.00144	4.666
	55.0	1.6300	2.38	0.00141	5.418
KCN at 15°	3.25	1.0154	19.10	0.00208	0.508
	6.5	1.0316	9.80	0.00194	1.031

TABLE 6.—RESISTIVITY OF ELECTROLYTES.—*Continued.* KOHL-
RAUSCH & HOLBORN

	G. Salt per 100 g. of sol.	Specific gravity	Resistivity	Temp. coefficient	Gram equivalent per liter
AgNO ₃ at 18°	5	1.0422	39.47	0.00219	0.307
	10	1.0893	21.20	0.00218	0.642
	15	1.1404	14.78	0.00216	1.009
	20	1.1958	11.57	0.00213	1.410
	25	1.2555	9.53	0.00211	1.851
	30	1.3213	8.14	0.00210	2.338
	35	1.3945	7.17	0.00208	2.879
	40	1.4773	6.45	0.00206	3.485
	45	1.5705	5.88	0.00205	4.168
	50	1.6745	5.44	0.00206	4.940
	55	1.7895	5.09	0.00207	5.800
	60	1.9158	4.80	0.00210	6.780
KC ₂ H ₃ O ₂ at 18°	5	1.0228	29.03	0.00224	0.522
	10	1.0466	16.10	0.00220	1.069
	20	1.0960	9.62	0.00223	2.239
	30	1.1484	8.01	0.00232	3.519
	40	1.2028	7.97	0.00251	4.910
	50	1.2598	8.97	0.00277	6.430
	60	1.3152	11.94	0.00325	8.060
	70	1.3714	21.06	0.00411	9.810
CuSO ₄ at 18°	2.5	1.0246	92.4	0.00214	0.322
	5	1.0513	53.2	0.00217	0.661
	10	1.1073	31.4	0.00219	1.393
	15	1.1675	23.8	0.00232	2.202
	17.5	1.2003	21.9	0.00237	2.642

TABLE 7.—DEPOSITION BY IMMERSION. GORE'S ELECTRO-DEPOSITION, PAGE 7

Solution	Deposits on	Does not deposit on
SbCl ₃	Bi, brass, Germ. Ag, Pb, Sn, Zn.	Sb, Cu, Fe, Ni, Au, Pt, Ag.
BiCl ₃	Fe, Pb, Sn, Zn.	Sb, Bi, brass, Cu, Au, Pt, Ag.
CuSO ₄ , Cu(NO ₃) ₂	Fe, Pb, Sn, Zn.	Sb, Bi, Cu, Au, Ni, Pt.
CuCl ₂	Bi, Fe, Pb, Sn, Zn.	Sb, Cu, Au, Ni, Pt, Ag.
Ammoniacal, CuCl ₂ .	Zn.	Sb, Bi, Cu, Fe, Au, Pb, Ni, Pt, Ag.
Hg NO ₃	As, Bi, Cd, Cu, Sb, Fe, brass, Pb, Zn.	
AgNO ₃	Pb, Sn, Cd, Zn, Cu, Bi, Sb, Fe, Ni.	Ag, Au, Pt.
Alcoholic AgNO ₃	As, Sb, Bi, Zn, Sn, Cu.	Fe.
AgCN.KCN	Zn, Pb, Cu, brass, Ger. Ag.	Sb, Bi, Sn, Fe, Ni, Ag, Au, Pt.
Au(CN) ₃ .KCN	Zn, Cu, brass, Ger. Ag.	Sb, Bi, Sn, Pb, Fe, Ni, Ag, Au, Pt.

TABLE 8.—POTENTIALS OF METALS IN THEIR NORMAL SALTS.
NEUMANN

	Sulphate	Chloride	Nitrate	Acetate
Magnesium	+1.239	+1.231	+1.060	+1.240
Aluminum	+1.040	+1.015	+0.775	
Manganese	+0.815	+0.824	+0.560	
Zinc	+0.524	+0.503	+0.473	+0.522
Cadmium	+0.162	+0.174	+0.122	
Iron	+0.093	+0.087		
Cobalt	-0.019	-0.015	-0.078	-0.004
Nickel	-0.022	-0.020	-0.060	
Tin		-0.085		
Lead		-0.095	-0.115	-0.079
Hydrogen	-0.238	-0.249		-0.150
Bismuth	-0.490	-0.315	-0.500	
Antimony		-0.376		
Arsenic		-0.550		
Copper	-0.515		-0.615	-0.580
Mercury	-0.980		-1.028	
Silver	-0.974		-1.055	-0.991
Palladium		-1.066		
Platinum		-1.140		
Gold		-1.356		

TABLE 9.—ELECTRODE POTENTIALS—CALCULATED BY THOMSON'S
RULE. WILSMORE

K	(+3.20)	(+2.92)	Pb	+0.148	-0.129
Na	(+2.82)	(+2.54)	H	0.0	-0.277
Ba	(+2.82)	(+2.54)	Cu	-0.329	-0.606
Sr	(+2.77)	(+2.49)	As	< -0.293	< -0.570
Ca	(+2.56)	(+2.28)	Bi	< -0.391	< -0.668
Mg	(+2.54)	(+2.26)	Sb	< -0.466	< -0.743
Mg	+1.491?	+1.214?	Hg	-0.750	-1.027
Al	+1.276?	+0.999?	Ag	-0.771	-1.048
Mn	+1.075	+0.798	Pd	< -0.789	< -1.066
Zn	+0.770	+0.493	Pt	< -0.863	< -1.140
Cd	+0.420	+0.143	Au	< -1.079	< -1.356
Fe	+0.340	+0.063	Cl	-1.417	-1.694
Co	+0.232	-0.045	Br	-0.993	-1.270
Ni	+0.228	-0.049	I	-0.520	-0.797
Sn	< +0.192	< -0.085	O	-1.119?	-1.396?

< indicates less than normal ionic concentration.

TABLE 10.—APPROXIMATE POTENTIALS IN VARIOUS ELECTROLYTES¹³

N.NaCl	N.KCN	$\frac{N}{2}$ K ₂ Cr ₂ O ₇	N.K ₂ S	N.NH ₄ -CNS	N.(NH ₄) ₂ -C ₂ O ₄	N.KOH
Mg +1.14	Al +1.06	Mg +.98	Mg +.80	Mg +1.19	Zn +.65	Al +1.06
Mn .60	Zn .90	Mn .35	Cu +.41	Mn .65	Mn .62	Mg .90
Zn .53	Mg .86	Zn .29	Mn .32	Zn .60	Cd .30	Zn .90
Al .30	Cu .81	Al .14	Cd .31	Cd .40	Al .24	Sn .63
Pb +.04	Mn .65	Cd +.08	Ag .20	Fe .15	Pb .07	Mn .42
Fe -.04	Cd .64	Pb -.08	Zn .19	Sn .02	Sn +.06	Cd .36
Sn -.07	Monel .38	Sn -.15	Al .15	Cu +.01	Ni -.05	Pb .28
Cr -.17	Ni .36	Fe -.30	Sn .11	Pb .00	Nichrome	Fe .27
					-.08	
Bi -.24	Au .34	Sb -.31	Cr .07	Ni -.07	Cr -.19	Bi .04
Sb -.29	Sn .30	Cu -.40	Au .05	Si -.24	W -.21	Mo +.01
Cu -.31	Nichrome	Mo -.40	Ni .05	Ag -.25	Fe -.26	Si -.04
	.30					
Mo -.35	Ag .28	Si -.45	Monel .04	Sb -.28	Cu -.30	Ni -.06
Ni -.37	Pb .15	Bi -.51	Te +.03	Bi -.34	Bi -.31	Cr -.10
W -.38	Sb .13	Ag -.62	Pt .03	Mo -.37	Monel	Cu -.14
					-.34	
Ag -.50	Hg .12	Cr -.62	Bi .03	Pt -.42	Mo -.38	C -.25
Te -.62	Cr .11	Hg -.62	Nichrome	Cr -.56	Ag -.48	Ag -.33
			+.03			
Au -.62	Si +.07	W -.62	Pb +.03	C -.60	C -.48	Au -.33
Pt -.63	Bi -.08	Nichrome	W +.02		Te -.53	Pt -.37
		-.66				
C -.63	W -.08	Monel .67	C -.01		Au -.53	
	Pt -.08	Ni -.74	Si -.01		Pt -.54	
	Fe -.12	C -.81	Fe -.07			
	Te -.13	Pt -.93	Mo -.11			
	Mo -.14	Te -.93	PbO ₂ -.60			
	C -.36	Au -.93				
	PbO ₂ -.68					

¹³ The values given in this table are the average results obtained by students, and are probably seriously in error in many instances. Although the order of the elements is more reliable than the numerical values, even this cannot be absolutely relied upon. The author will appreciate corrections and additions to the data set forth in the table.

TABLE 11.—DECOMPOSITION VOLTAGE. LE BLANC

H ₂ SO ₄	1.67 volt	SrCl ₂	2.01
HNO ₃	1.69	BaCl ₂	1.95
H ₃ PO ₄	1.70	ZnSO ₄	2.35
HCl	1.31	ZnBr	1.80
NaOH	1.67	NiSO ₄	2.09
KOH	1.69	NiCl ₂	1.84
NH ₄ OH	1.74	AgNO ₃	0.70
Na ₂ SO ₄	2.21	CdSO ₄	2.03
NaNO ₃	2.15	CoSO ₄	1.92
NaCl	1.98	HgCl ₂	1.30
NaBr	1.58	Fe ₂ (SO ₄) ₃	1.62
NaI	1.12	FeSO ₄	2.02
NaC ₂ H ₃ O ₂	2.10	AuCl ₃	0.39
K ₂ SO ₄	2.20	FeCl ₂	2.16
KNO ₃	2.17	SnCl ₂	1.76
KCl	1.96	MnSO ₄	2.60
(NH ₄) ₂ SO ₄	2.11	MnCl ₂	2.77
CaCl ₂	1.89	CuCl ₂	1.36



INDEX

- Addition agents 84, 89
- Alloys, electrodeposition of, 65
 - 97, 101, 113-115
- Aluminum electrodes, 29
 - corrosion of, 70, 112
 - electroplating of, 110, 111
 - rectifier, 29
- Ammonium persulphate, 126
- Atomic weight, table of, 138
- Barium perchlorate, 131
- Brass plating, 60, 66, 97-101, 107, 108, 113
- Calomel electrode, 36, 39
- Chlorates, preparation of, 127, 128
- Coloring metals, 118, 119
- Copper plating, 95-97, 104, 110, 111, 113
- Corrosion of metals, 60-62
- Coulombmeter, 30, 31, 111
- Critical current density, 107
- Current efficiency, 30, 111, 112
- Decomposition voltage, see "E.M.F. of decomposition."
- Deposition by immersion, 103
 - of metals, see "Electrodeposition."
- Discharge potential, 56-57
- Electrical instruments, principles of construction, 7
 - protection from injury, 8
- Electric cleaning of metals, 60, 91
- Electrochemical equivalents, 138
- Electrode, aluminum, 29, 70, 112
 - intermediate, 69
 - normal calomel, 36, 39
- Electro-deposition of alloys, 97-101
 - of brass, 66, 97-101, 113
 - of cadmium, 116
 - of copper, 68, 95-97, 104, 110, 111, 113
 - of lead, 12, 113
 - of iron, 116
 - of nickel, 68, 93-95, 104, 105, 108, 109, 111, 112
 - of silver, 97, 101, 102, 105, 115
 - principles of, 84-89
- Electrolytic analysis, 66
 - oxidation, 121, 122, 124-132, 133, 135, 136
 - reduction, 11, 33, 121-123
 - separation of metals, 63
- Electromotive force, 33, 34
 - of decomposition, 43
 - of copper sulphate, 49
 - of hydrochloric acid, 48, 50
 - of nitric acid, 48, 50
 - of sodium chloride, 43
 - of sulphuric acid, 47, 48, 50
 - of zinc bromide, 46, 50

- Electromotive force, effect of electrodes of unequal size upon, 49-55
 table of numerical values, 145
- Faraday's law, 29
- Fig. 1—Resistivity of electrolytes, 14
- 2—Resistivity, using a low-scale voltmeter, 17
 - 3—Resistivity using a double-scale voltmeter, 18
 - 4—Resistivity, of wire, 19
 - 5—Resistivity, with voltmeter only, 21
 - 6—Resistivity, by voltmeter and resistance box, 22
 - 7—Cell for temperature coefficient of resistance, 23
 - 8—Resistance of a fused electrolyte, 25
 - 9—Potentiometer and connections, 38
 - 10—Polarization in a voltaic cell, 42
 - 11—E.M.F. of decomposition, 43
 - 12—E.M.F. of decomposition and polarization, 45
 - 13—E.M.F. of decomposition and polarization by the potentiometer, 51
 - 14—Curves of polarization at electrodes, 53
 - 15—Curves for electrodes of unequal size, 54
- Fig. 16—Apparatus for electrolytic analysis, 67
- Galvanite plating, 105
- Galvanometer key, special, 52
- Galvanoplasty, 119
- Gas volumes, reduction to standard conditions, 32
- Hypochlorite of sodium, 135
- Instruction for students, 5
- Laboratory equipment, 2
- Lead nitrate, electrolysis of, 12
- Mercury cathode, 12
 refining of, 134
- Metallochromes, 118
- Nickel plating, 93-95, 104, 105, 108, 109, 111, 112
- Ohm's law, 14
- Overvoltage, 58
 of hydrogen, 58, 121
 of oxygen, 122
- Oxidation, 121, 122, 129-132, 133, 135, 136
- Oxidizing metals, baths for, 80-82
 experiments, 118-119
- Passive state of metals, 58-60
- Perchlorates, 130, 131
- Persulphates, estimation of, 126
 preparation of, 125-127
- Plating baths, composition of, 72-79
 metal content and current density, 83

- Plating by contact, 104
by immersion, 103
general principles, 84-89
- Polarization, 15
effect of size of electrodes
on, 49, 55
measurement of, 17, 44-48
- Polishing metals, 92
- Potassium, 137
bromate, 128
bromide, 11, 128
chlorate, 127
chloride, electrolysis of,
63, 127
chromate, 133
ferrocyanide, 136
iodate, 129
perchlorate, 130
permanganate, 133
persulphate, 125
- Potential, 33-41
of electrodes, measurement
of, 39-41
- Potentiometer, 37
- Quicking, 101
- Reduction, electrolytic 11, 33,
121-123
- Resistance, measurement of
13-22
of a fused electrolyte, 25
of glass, effect of heat
upon, 26
of primary cells, 28
of storage cells, 28
of a voltmeter, 20
temperature coefficient of,
19, 23
- Resistivity, 13
effect of the solvent upon,
24
- Resistivity of copper sulphate,
15, 17, 19
of metals, 18, 139
of plating baths, 19
- Scheele's green, 134
- Separation of metals, electro-
lytic, 63
- Single potentials, 34-41, 143,
144
- Silver plating, 97, 101, 102, 105,
115
striking baths, 102
- Sodium chloride, electrolysis
of, 11, 12, 16, 135
hydrate, electrolysis of, 31
hypochlorite, preparation
of, 135
nitrate, electrolysis of, 11,
33
sulphate, electrolysis of, 63
- Specific resistance, see "Resis-
tivity."
- Spotting out of plated articles,
97
- Switch-key, special, 52
- Table of atomic weights, 138
of decomposition voltage,
145
of deposition by immersion,
142
of electrochemical equiva-
lents, 139
of metal content of plating
baths, 83
of overvoltage of hydro-
gen, 121
of oxygen, 122
of plating baths metal con-
tent *vs.* current den-
sity, 83